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FUNDAMENTAL STUDY OF FACTORS INFLUENCING COLOR OF PORCELAIN ENAMELS*

By Ralph L. Cook and Andrew I. Andrews

Abstract

The fundamental basis of color specification, namely, brilliance, purity, and dominant wave length, has been determined from spectrophotometric curves by means of an integrating calculator. The effect of variations in the particle size of the frit and the coloring agents on the purity, brilliance, and dominant wave length has also been studied.

I. Introduction

In a previous investigation,[1] the effect of variations in the particle size of typical green and blue color stains in sized fractions of a representative clear frit was studied with respect to general observations from the spectrophotometric curves. The present studies show the effect of such variations on fundamental color properties, namely, brilliance, purity, and dominant wave length.

The use of the recording type of spectrophotometer has increased the desirability for a rapid method of calculating the tristimulus values for the fundamental specification of color. The selected ordinate method described by Hardy[2] considerably reduces the labor involved as compared to the older or weighted ordinate method. The process is simplified in the ordinate method to a basis where it consists essentially of adding the reflection values for the thirty selected ordinates for a specific illuminant and multiplying by appropriate factors.

Swank and Mellon,[3] with later modifications by Sears,[4] have described a type of calculator for obtaining the tristimulus values from spectrophotometric data. A modified integrating calculator* was constructed in order to obtain greater speed of operation with less fatigue to the operator as well as greater simplicity of design and construction (Fig. 1).

Fig. 1.—Calculator for determination of tristimulus values from spectrophotometric data.

The instrument is first calibrated by obtaining the reading of the counter and clutch scales for the 30 oscillations from zero to 100%. The X, Y, and Z series of angle members is necessary, with the proper selected ordinates marked off for the different standard illuminants. The graph paper with the desired spectrophotometric curve is clamped in position on the drum. A zero setting is made by placing the selected ordinate scale on the zero line of the graph paper and turning both the shaft and clutch counters to zero.

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* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 22, 1942 (Enamel Division). Received April 23, 1942.

[1] A. I. Andrews and R. L. Cook, "Relation of Particle Sizes of Frit and Color Oxides to Color Properties of Porcelain Enamels," *Jour. Amer. Ceram. Soc.*, **24** [9] 298–310 (1941).

[2] A. C Hardy, Handbook of Colorimetry. The Technology Press, Cambridge, Mass., 1936. 87 pp.

[3] H. A. Swank and M. G. Mellon, "Calculator for Obtaining Tristimulus Values from Spectrophotometric Data," *Jour. Optical Soc. Amer.*, **27**, 414–15 (1937); *Ceram. Abs.*, **17** [3] 110 (1938).

[4] F. W. Sears, "Improved Calculator for Obtaining Tristimulus Values from Spectrophotometric Curves," *Jour. Optical Soc. Amer.*, **29**, 77–78 (1939); *Ceram. Abs.*, **19** [4] 100 (1940).

* Constructed by J. O. Kraehenbuehl, Department of Electrical Engineering, University of Illinois, Urbana, Ill.

The drum is revolved with the left hand until the curve is in line with the first selected ordinate on the scale. The shaft is turned with the right hand until the extended rod comes up against the stop on the drum. The distance through which the shaft turns is a measure of the selected ordinate and is recorded on the small revolution counter operated by the shaft through an out-running clutch. The drum is moved to line up the spectrophotometric curve with the second selected ordinate, and this process is repeated for the thirty selected ordinates. The tristimulus values for X, Y, and Z for I.C.I. illuminant C were determined in the present work.

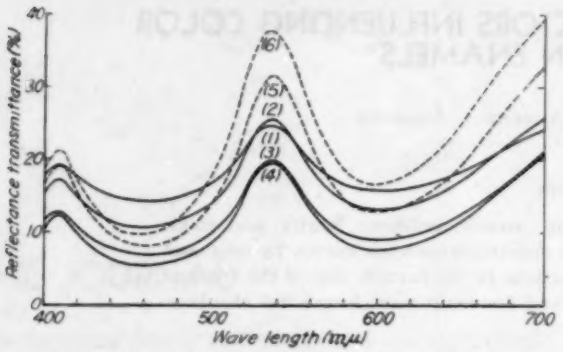

FIG. 2.—Frit particle, 45 to 75 μ, variable green color particle (65 gm. per sq. ft. over white).

Curve No.	Color particle (μ)	Brilliance	Purity	Dominant wave length
1	25–45	19.6	10.5	552
2	15–25	18.2	19.0	556
3	5–15	13.4	22.0	554
4	<5	12.4	27.0	555
5	0.5–1.0	20.3	31.5	557
6	0.0–0.5	25.3	34.0	559

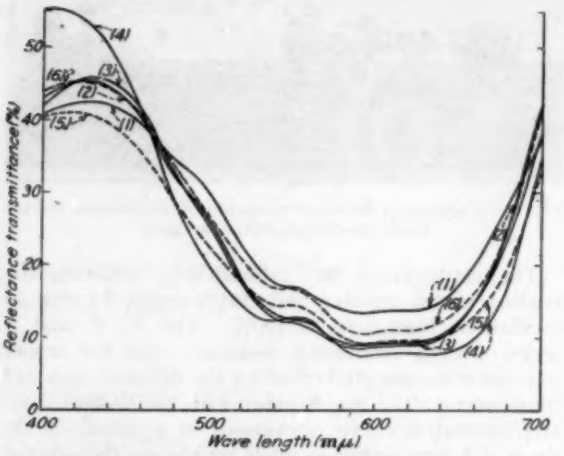

FIG. 3.—Frit particle, 45 to 75 μ; variable blue color particle (65 gm. per sq. ft. over white).

Curve No.	Color particle (μ)	Brilliance	Purity	Dominant wave length
1	25–45	18.9	40.0	473
2	12–25	14.7	52.0	471
3	5–15	14.2	54.0	471
4	<5	13.0	56.5	466
5	0.5–1.0	14.7	47.0	472
6	0.0–0.5	17.3	46.0	473

The advantage of this method is that the selected ordinate scale is always in contact with the curve, making it relatively easy to follow and eliminating the necessity of turning the drum back to zero for each new position. This type of clutch makes it possible to turn back the shaft to zero without moving the counter. A reading glass, which slides freely on an angular bar along the front of the instrument, is helpful in making settings, particularly for the Z function where the spacing of the selected ordinates is small.

II. Experimental Details

Selected color panels prepared in the previous investigation[1] were rerun on the General Electric recording spectrophotometer. The Kraehenbuehl integrating calculator* was used to determine the tristimulus values from the spectrophotometric curves.

The tristimulus values for I.C.I. illuminant C, using the thirty selected ordinates, were determined by the method outlined by Hardy.[2] The trichromatic coefficients were calculated from the tristimulus values by using equations (1), (2), and (3).

$$x = \frac{X}{X + Y + Z} \tag{1}$$

$$y = \frac{Y}{X + Y + Z} \tag{2}$$

$$z = \frac{Z}{X + Y + Z} \tag{3}$$

x, y, and z = trichromatic coefficients.
X, Y, and Z = tristimulus values.

Because of the proper selection of the primary functions and in order to avoid negative tristimulus values, the Y values represent the relative brilliance. The values for purity and dominant wave length are determined by reference to suitable graphical chromaticity diagrams.

III. Results

(1) Variable Size Color Particle

The spectrophotometric curves in Fig. 2 show the effect of variable green color particles with a constant

*See star (*) reference, p. 73.

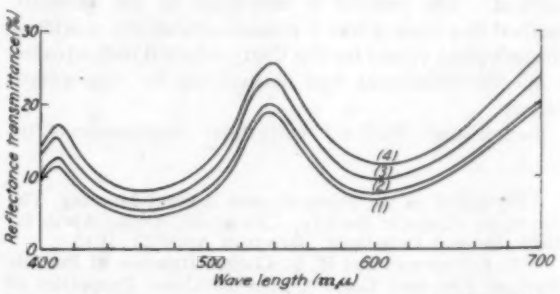

FIG. 4.—Green color particle, <5 μ; variable frit particle (65 gm. per sq. ft. over white).

Curve No.	Frit particle (μ)	Brilliance	Purity	Dominant wave length
1	45–75	12.4	27.0	555
2	15–25	12.5	28.7	556
3	5–15	15.1	27.0	556
4	<5	17.5	24.0	557

relatively large frit particle and also the results for the brilliance, purity, and dominant wave length for each curve. The values of brilliance decreased to particles of less than (>) 5 microns and then increased rapidly. The purity of this color increased progressively as the particle size of the colorant decreased, and the dominant wave-length value showed a general increase from 552 to 559.

The spectrophotometric curves in Fig. 3 show the effect of the variable blue color particles in the 45- to 75-micron frit particles. The brilliance of this series decreased down to the particles of less than 5 microns and then increased; the purity of the color also increased to the <5-micron fraction and then decreased; but the dominant wave-length values decreased from 473 to 466 for the <5-micron particles and then increased to 473 as the particle size of the colorant was further decreased.

(2) Variable Size Frit Particle

The group of curves in Fig. 4 represents the <5-micron green color fraction with variable frit particles. The respective values show that (*a*) the brilliance increased with decreasing frit particle size, (*b*) the purity decreased slightly as the frit particle size was decreased from the 5- to 15-micron fraction to the <5-micron fraction, and (*c*) the dominant wave-length value showed a slight increase.

Figure 5 shows the spectrophotometric curves and the corresponding values for each curve. The brilliance again increased as the frit particle size decreased, and the purity showed a considerable drop from 56.5 for the 45- to 75-micron fraction to 34.0 for the <5-micron fraction. The dominant wave length showed a sharp initial change but remained practically constant as the frit particle size was decreased.

(3) Variable Weight of Application

The curves and data in Fig. 6 show the effect of variations in the weight of application of the green color particle on brilliance, purity, and dominant wave length. In this particular case, the brilliance and purity decreased, but the dominant wave-length value remained essentially constant as the weight of enamel applied was increased. Particularly in the lighter applications, the white enamel underneath had an appreciable effect on the resulting color.

With the blue enamel (Fig. 7), the brilliance decreased considerably, the purity increased, and the

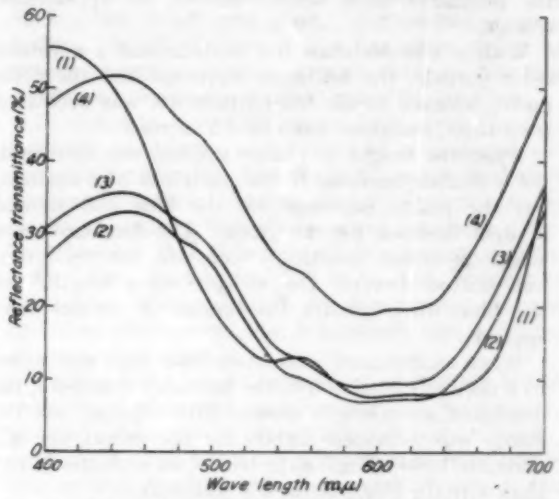

FIG. 5.—Blue color particle, <5 μ; variable frit particle (65 gm. per sq. ft. over white).

Curve No.	Frit particle (μ)	Brilliance	Purity	Dominant wave length
1	45–75	13.0	56.5	466
2	15–25	12.6	54.0	476
3	5–15	15.0	46.0	475
4	<5	26.8	34.0	475

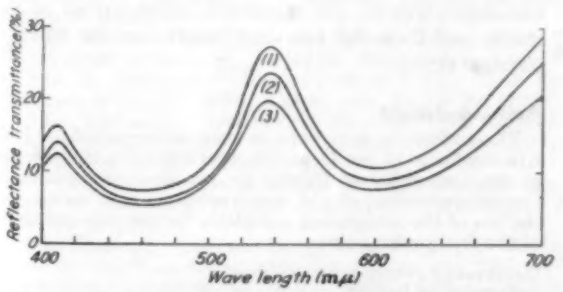

FIG. 6.—Variable weight of application; green color particle, <5 μ; frit particle (45 to 75 μ over white).

Curve No.	Weight (gm./sq. ft.)	Brilliance	Purity	Dominant wave length
1	30	17.1	30.0	556
2	45	14.6	29.5	556
3	65	12.4	27.0	555

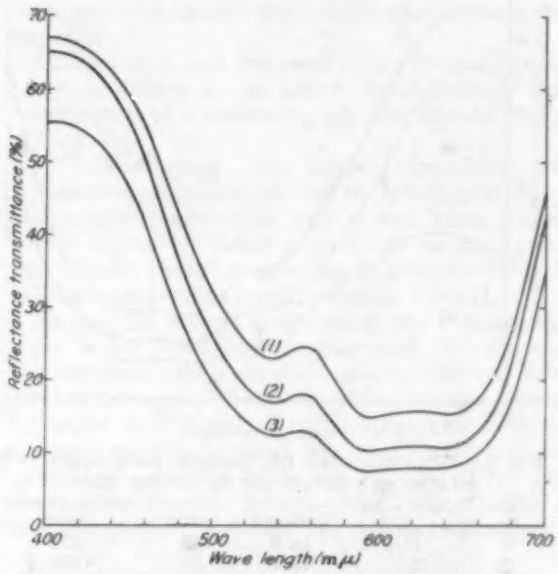

FIG. 7.—Variable weight of application; blue color particle, <5 μ; frit particle (45 to 75 μ over white).

Curve No.	Weight (gm./sq. ft.)	Brilliance	Purity	Dominant wave length
1	30	23.5	49.0	472
2	45	17.7	53.0	470
3	65	13.0	56.5	466

dominant wave length showed a slight change from 472 to 466 as the weight of application was increased.

(4) Variable Percentage of Colorant

Figures 8 and 9 show the general effect of increased percentages of the colorant. The spectrophotometric curves and data in Fig. 8 show the effect of 1½, 3, and 6% of the 5- to 15-micron fraction of the green color oxide in an unsized frit ground to 10% of residue on a No. 200 sieve. In this case, the brilliance decreased, the purity of the color increased, and the dominant wave length remained essentially the same as the amount of colorant added was increased. The curves in Fig. 9 show the results of variable percentages of the <5-micron blue fraction in the unsized frit; the brilliance decreased, the purity was highest with the 3% addition of the blue oxide, and the dominant wave length showed no appreciable change as the percentage of color oxide was increased.

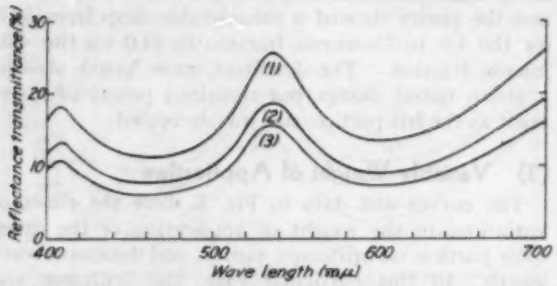

FIG. 8.—Green color oxide frit (variable percentage); 10% on 200-mesh (65 gm. per sq. ft. over white).

Curve No	Color oxide (%) (5–15 μ)	Brilliance	Purity	Dominant wave length
1	1½	18.5	16.5	554
2	3	13.1	17.5	552
3	6	10.8	19.0	553.5

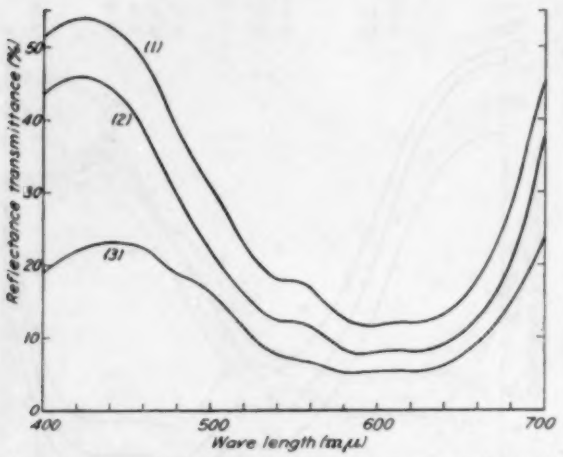

FIG. 9.—Blue color oxide frit (variable percentage); 10% on 200-mesh (65 gm. per sq. ft. over white).

Curve No.	Color oxide (%)	Brilliance	Purity	Dominant wave length
1	1½	18.9	49	472
2	3	13.3	55	470
3	6	8.6	50	473

IV. Summary of Results

By the use of an integrating calculator, the fundamental color values of brilliance, purity, and dominant wave length can be readily and rapidly determined.

With a constant frit particle and a variable-sized color particle, (*a*) the brilliance decreased to the <5-micron fraction and then increased, (*b*) the purity of the blue color reached a maximum with the <5-micron fraction and that of the green color increased progressively down to the smallest fraction, and (*c*) the dominant wave length showed no appreciable change.

With a variable-sized frit particle and a constant color particle, the brilliance increased and the color purity lessened as the frit particle size was decreased from 45 to 75 microns down to <5 microns.

When the weight of enamel applied was increased, the brilliance decreased in the green and blue enamels, but the purity increased for the blue and showed a slight decrease for the green. The dominant wave length remained practically constant for the green but shifted toward the shorter wave lengths for the blue when greater thicknesses of enamel were applied.

When an increased amount of color stain was added to a normally ground frit, the brilliance decreased, the dominant wave length showed little change, and the purity was increased slightly for the green; the 3% addition, however, gave the blue stain a greater purity than with the 1½% or the 6% additions.

In studying colors, the term "brilliance" is rather misleading, inasmuch as the more efficient colorants have a relatively low brilliance. The purity of a colorant varies widely, depending on the particle size of the frit and of the added color stain. The values for the purity of the blue color stain, in general, were much higher than those for the chrome green base color stain. The dominant wave length, as expected, was dependent on the respective compositions of the stains, and these did not vary greatly for the differing physical states.

Acknowledgment

The authors wish to express their appreciation to J. O. Kraehenbuehl of the Department of Electrical Engineering at the University of Illinois for his kind cooperation in the determination of the spectrophotometric curves and the use of the integrating calculator for the determination of the tristimulus values.

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EFFECTS OF LITHIA SUBSTITUTION FOR SODA IN VITREOUS ENAMEL*

By Marvin O. Lewis

Abstract

Lithia, as lithium carbonate, was substituted progressively for soda in the composition of a white cover frit. Substitutions were made on both weight and mol bases.

Mol replacement of soda by lithia has resulted in improved fusibility, gloss, and opacity; higher gouge, surface abrasion, and acid resistance; and lower thermal expansion coefficient. Weight replacement has caused increased fusibility and gloss; a small decrease in surface abrasion resistance; marked decreases in opacity and in gouge and acid resistance; little change in thermal expansion coefficient, and a noticeable lowering of the transformation temperature.

I. Introduction

Lithia is used as a minor constituent of some opal, special bottle, and fiber types of glasses, some vitrifiable color fluxes and glazes, and certain ceramic bodies. In all of these, it is a flux often producing lower thermal expansion, greater acid or corrosion resistance, increased workability, and higher gloss.

D'Adrian[1] patented its use in 1923 in the form of lepidolite as a fluxing constituent of ground-coat and cover-coat enamels; Malinovzsky[2] reported that it does not increase adherence; McIntyre[3] recommended its use to obtain a high coefficient of expansion; Vielhaber[4] stated that it has no effect on opacity but is a good flux; Staley[5] found it to be unsatisfactory in developing acid resistance in dry-process enamels; and Stuckert[6] reported that it increased acid resistance of wet-process enamels.

Hodkin and Cousen[7] have found that lithia lowers viscosity of glass and thus increases the tendency to devitrify; Charrin[8] reported that it reduces viscosity, produces a more corrosion-resistant glass, and that it also reduces thermal expansion; and Waterton and Turner[9] reported in 1935 that the substitution of lithia for soda in a soda-lime-silica glass increases thermal expansion. Navias[10] has reported that, in borate and borosilicate compositions, lithia has essentially the same effect on expansion as its mol equivalent of soda, and he commented on the low viscosity and short working range of lithium-containing glasses.

II. Experimental Work

(1) Preparation of Enamels

(*A*) *Lithium Material:* Several lithium minerals are available for commercial use, namely, amblygonite, a complex lithium-aluminum fluophosphate assaying about 8% of lithia; spodumene, a lithium-aluminum silicate containing about 6% of lithia; and lepidolite, a complex lithium-aluminum fluosilicate with approximately 4% of lithia. These raw materials, however, are not particularly uniform in composition and sometimes contain undesirable amounts of chromogenic impurities.

Lithium carbonate was used as the lithium-bearing batch constituent in the present investigation. This material was of a technical grade and assayed 97.7% of Li_2O.

(*B*) *Compositions:* The initial composition was a plant-proved, general-purpose frit which produced a moderately opaque white cover enamel when applied over a commercial cobalt ground coat on sheet steel. The original melted composition is given in Table I, and the corresponding batch formula in Table II.

Because the sodium combined in the feldspar and borax is not available for replacement, this formula was rewritten, and boric acid and soda ash were substituted for borax. From this second formula, identical to the first in melted composition, two series of compositions were prepared, one on a weight replacement basis in which lithia was substituted for one fourth, two fourths, three fourths, and all of the available weight of soda; and one on a mol replacement

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* Presented at the Forty-Second Annual Meeting, The American Ceramic Society, Toronto, Canada, April 9, 1940 (Enamel Division). Received June 9, 1942.

Based on a thesis submitted by the writer in partial fulfillment of the requirements for the degree of Master of Science in Ceramics at Rutgers University, New Brunswick, N. J., June, 1940.

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[9] S. C. Waterton and W. E. S. Turner, "Properties of Mixed Alkali-Lime-Silica Glasses Containing Lithia, Soda, Potash, and Rubidia," *Jour. Soc. Glass Tech.*, **18** [72] 268–85 (1934); *Ceram. Abs.*, **14** [8] 186 (1935).

[10] Louis Navias, "Effect of Lithium Oxide on Thermal Expansion of Glass," *Jour. Amer. Ceram. Soc.*, **18** [7] 206–10 (1935).

TABLE I

MELT COMPOSITIONS

(Weight Percentage Calculated from Batch Formulas)

Sample No.	Original formula 01 and 02	Weight replacement series W14	W24	W34	W44	Mol replacement series M13	M23	M33
B_2O_3	9.9	9.9	9.9	9.9	9.9	10.1	10.3	10.5
Al_2O_3	3.9	3.9	3.9	3.9	3.9	4.0	4.1	4.1
SiO_2	44.5	44.5	44.5	44.5	44.5	45.4	46.2	47.1
Li_2O		2.65	5.3	7.95	10.6	1.7	3.5	5.4
Na_2O	11.2	8.55	5.9	3.25	0.6	7.8	4.3	0.7
K_2O	2.4	2.4	2.4	2.4	2.4	2.4	2.5	2.5
CaF_2	4.5	4.5	4.5	4.5	4.5	4.6	4.7	4.8
Na_3AlF_6	11.5	11.5	11.5	11.5	11.5	11.7	11.9	12.2
ZnO	4.0	4.0	4.0	4.0	4.0	4.1	4.2	4.2
$NaSbO_3$	8.0	8.0	8.0	8.0	8.0	8.2	8.3	8.5

TABLE II

BATCH FORMULAS

Na_2O replaced →	Original formula None		Weight replacement series 1/4	1/2	3/4	All	Mol replacement series 1/2	3/2	All
	01	02	W14	W24	W34	W44	M13	M23	M33
Feldspar	24.0	24.0	24.0	24.0	24.0	24.0	24.0	24.0	24.0
Flint	27.5	27.5	27.5	27.5	27.5	27.5	27.5	27.5	27.5
Borax	27.1								
Boric acid		17.6	17.6	17.6	17.6	17.6	17.6	17.6	17.6
Lithium carbonate			6.5	13.1	19.6	26.2	4.2	8.4	12.6
Sodium carbonate	8.3	15.9	11.4	6.9	2.4		8.8	3.8	
Sodium nitrate	3.5	3.5	3.5	3.5	3.5		3.5	3.5	
Fluorspar	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Cryolite	11.5	11.5	11.5	11.5	11.5	11.5	11.5	11.5	11.5
Zinc oxide	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Sodium antimonate	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0

basis in which lithia was substituted for one third, two thirds, and all of the available mols of soda. These compositions were designated in the weight replacement series as W14, W24, W34, and W44; in the mol replacement series, as M13, M23, and M33; and the two original formulas, alike in melted composition, were termed 01 and 02. These compositions are given in Table I and the batch formulas in Table II.

(*C*) *Smelting and Milling:* The batches, approximately 14 kg. each, were smelted in an oil-fired rotary smelter. The frits were ground in jar mills, using the following formula and corresponding mill charge:

	Mill formula	Mill batch (gm.)
Frit	100	1000
Tin oxide	6	60
Enamel clay	6	60
Magnesium carbonate	1/4	2.5
Water	45	450

The fineness of milling was determined by the standard screen test for wet-milled enamels.* The slips were milled carefully to 2 ± 0.2 gm.; this 0.2-gm. limit was maintained because, in this range of fineness, a 0.1-gm. difference would account for a change of nearly 0.04% of reflectance.

(*D*) *Preparation of Specimens:* Sheet-steel plates and pans for test specimens, the sizes and gauges of which are described in the respective tests, were commercially ground coated in accordance with general industrial practice.

The enamel slips were aged at least one week and were set up as they were needed with small additions of calcium chloride in saturated solution. The enamels in the weight replacement series required the largest additions.

The specimens were sprayed (the weights of application are described in section (2) under individual tests) and fired in a gas-fired muffle furnace for 1 minute and 35 seconds at 1510°F. Inasmuch as the weights of rectangular plates, square plates, and pans were substantially the same and the enamels appeared to be well fired, no attempt was made to alter these conditions for the different shapes.

(2) Tests and Results

(*A*) *Relative Fusibility:* Fusion blocks of the type commonly employed for feldspar fusibility determinations were used to measure this property. Each block was laid back horizontally, a dam of unglazed porcelain tile was wired across the opening nearest the graduated slope, and the space thus provided was filled with frit grains sized to plus 20-minus 60-mesh. The grains were carefully vibrated into place by gently tapping the block; this method was used in the preparation of each block.

Four blocks at a time, still in horizontal position and at room temperature, were placed in a Nichrome-wound electric muffle furnace. The temperature was increased

* Tentative Screen Test for Wet-Milled Porcelain Enamels. Porcelain Enamel Institute, November, 1938.

on a definite, reproducible heating schedule of approximately 10°F. per minute to 1200°F.; the current was then cut off, and the furnace was permitted to cool to room temperature. After this sintering operation, the dams were removed and two blocks at a time were placed upright in the furnace and the temperature was again increased on the established heating schedule. The fusion of the frit grains was observed through a port in the furnace door, and the temperatures were recorded when the flow passed the first mark at the top of the slope and the last mark at the bottom.

The data recorded for each run were plotted against the percentage of lithia in the composition (Fig. 1). These curves show that the substitution of lithia for soda on a weight basis lowers by some 100°F. the temperature at which appreciable flow takes place and that substitution on a mol basis effects a lowering of about 20°F. These effects were greatest when lithia and soda were present in approximately equal amounts. Extreme replacement on a mol basis resulted in little change in temperature of either initial or final flow. Extreme replacement on a weight basis, however, raised the temperature of initial flow until it almost coincided with that of final flow; that is, the frit had a softening temperature almost as high as that of the original composition, but when softening took place, the viscosity was so low that flow was very rapid.

(*B*) *Thermal Expansion:* The thermal expansion specimens were prepared by the Andrews and Howe method.[11] Melts were made of frits 02, W44, and M33 in a platinum crucible in an upright electric furnace. Rods, about 4 mm. in diameter, were readily drawn from the melts of frits 02 and M33, but they were drawn from W44 with considerable difficulty because of the short working range of this glass. These rods were annealed in an electric muffle furnace at temperatures at which fine glass fibers just deformed when they were laid on pieces of unglazed tile with a 2-cm. length projecting cantileverwise. The rods were held at the annealing temperature for at least two hours and were cooled through the first 100° at about 0.1°C. per minute and to room temperature at about 2.0°C. per minute. Three solid cones, about 5 mm. high, were cut from each rod.

Actual expansion measurements were made by the Fizeau interferometric method[12] described by Merritt[13] for application to ceramic materials, and Saunders'[14] improved procedures were also incorporated.

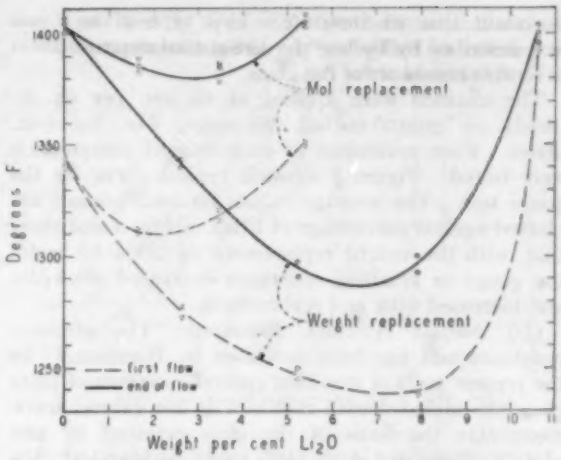

FIG. 1.—Fusibility curves, flow temperature vs. lithia content.

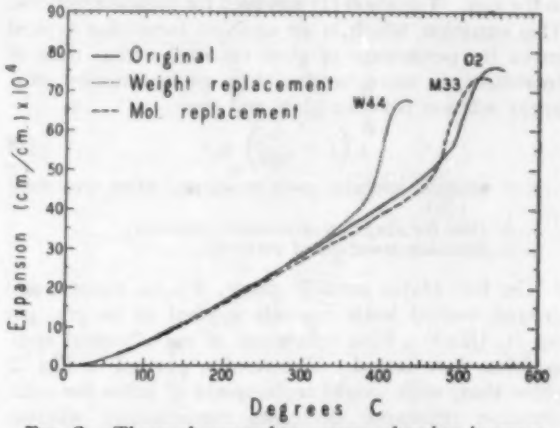

FIG. 2.—Thermal expansion curves, showing increase in length with temperature, for the original composition and the two extreme replacement compositions.

The expansion data, plotted against temperature (Fig. 2), show that weight replacement of soda by lithia to approximately 10% of the composition effected little change in the expansion coefficient up to 300°C. but lowered the transformation temperature about 100°C. Replacement of soda by an equivalent number of mols of lithia to about 10% of the composition weight resulted in a slight lowering of the expansion coefficient up to 450°C. and lowered the transformation temperature only 15°C.

(*C*) *Gouge Resistance:* The test used was one still in process of development by the National Bureau of Standards[15] in a cooperative program with the

[11] A. I. Andrews and E. E. Howe, "Effect of Fluorides on Properties of White Sheet-Iron Enamels," *Jour. Amer. Ceram. Soc.*, **17** [10] 288–91 (1934).

[12] L. Fizeau, "Use of Interferometer for Expansion Measurement," *Ann. Phys.*, **128**, 564 (1866).

[13] (*a*) G. E. Merritt, "Application of Interferometer to Measurements of Thermal Dilatation of Ceramic Materials," *Bur. Standards Sci. Paper*, No. 485, 17 pp., 1924; *Ceram. Abs.*, **3** [6] 200 (1924).

(*b*) G. E. Merritt, "Interference Method of Measuring Thermal Expansion," *Bur. Standards Jour. Research*, **10** [1] 59–76 (1933); R.P. 515; *Ceram. Abs.*, **12** [3] 129 (1933).

[14] J. B. Saunders, "Improved Interferometric Procedure with Application to Expansion Measurements," *Jour. Research Nat. Bur. Standards*, **23** [1] 179–95 (1939); R.P. 1227; *Ceram. Abs.*, **18** [11] 306 (1939).

[15] (*a*) W. N. Harrison and L. Shartsis, "Experimental Work on Crushing Resistance of Enamels," *Bur. Standards Tech. News Bull.*, No. 258, October, 1938.

(*b*) "Test for Resistance of Porcelain Enamels to Gouging," 12 pp., July, 1942. Porcelain Enamel Institute, Inc., Chicago, Ill., Product Standards Section, Washington, D.C.; *Ceram. Abs.*, **22** [1] 5 (1943).

(*c*) "G. H. Spencer-Strong and W. G. Cooper, "Gouge Resistance of Porcelain Enamels" *Jour. Amer. Ceram. Soc.* **26** [1] 1–4 (1943).

Porcelain Enamel Institute. This type of test was first described by Bailey[16] for the partial determination of scratch resistance of flat glass.

The enamels were applied at 66 gm. per sq. ft. (fired) on ground-coated, 20-gauge, 4-in. by 6-in. plates. Four specimens of each enamel composition were tested. Figure 3 shows a typical curve for the gouge test. The average values for each enamel are plotted against percentage of lithia in Fig. 4 and show that, with the weight replacement of lithia for soda, the gouge or crushing resistance decreased markedly and increased with mol replacement.

(*D*) *Surface Abrasion Resistance:* The abrasion resistance test has been described by Harrison.[17] In the present tests, a standard control specimen of plate glass was included with each run of five enamel specimens. On the basis of the gloss retained by this plate as compared with 50% taken as standard, the values were corrected for each of the five plates used in the run. Equation (1) was used for these corrections. This equation, which is an analytic form of a typical curve for percentage of gloss retained versus time of treatment, is more precise than an assumption of a linear relation between gloss and time.

$$g\left(t + \frac{c}{100}\right) = c \qquad (1)$$

g = original specular gloss remaining after treatment (%).
t = time for abrasion treatment (minutes).
c = abrasion constant of material.

The test plates were 18 gauge, $4^3/_4$ in. square, and ground coated with enamels applied at 66 gm. per sq. ft. (fired). Five specimens of each enamel composition were tested. The results, plotted in Fig. 5, show that, with weight replacement of lithia for soda, abrasion resistance decreases continuously whereas with mol replacement it increases.*

(*E*) *Gloss:* The initial gloss readings, made on the surface abrasion test specimens and corrected for small inaccuracies[17] in the gloss scale of the reflectometer, were averaged and plotted (Fig. 6). These curves indicate an increase in specular gloss in both series of enamels; a maximum gloss was reached at about 3% of lithia in the weight replacement series, but the increase was greater and continuous to the full replacement of soda in the mol basis series. In practical terms, however, this improvement in gloss is small.

(*F*) *Reflectance:* A Hunter reflectometer,[18] calibrated with Bureau of Standards standard reflectance plates as specified by the Porcelain Enamel Institute,† was used to measure the apparent reflectance of five or more specimens of each enamel composition.

Enamels were prepared as previously described and sprayed on 20-gauge, 4-in. by 6-in., ground-coated plates at application weights of approximately 45, 67, and 80 gm. per sq. ft. (fired); weighings of plates were made to ±0.01 gm., that is, ±0.06 gm. per sq. ft.

Reflectance values versus application weight were plotted for each specimen, and curves were drawn for each enamel composition (Fig. 7). From the curve for each composition, the reflectance was taken corresponding to 65-gm. per sq. ft. application and plotted against lithia content (Fig. 8). These curves reveal that reflectance decreased continuously with the

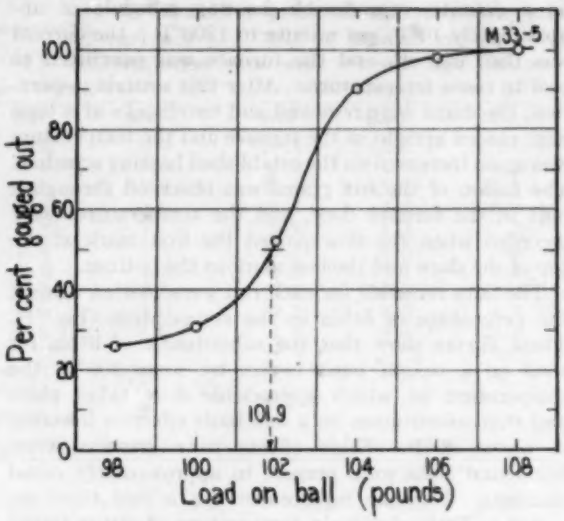

FIG. 3.—Typical curve for gouge test in which percentage of enamel gouged out is plotted against load on the ball; shows method by which gouge value may be determined.

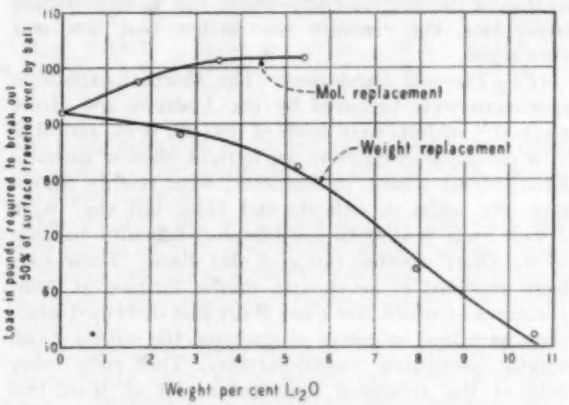
Load in pounds required to break out 50% of surface traveled over by ball
Mol. replacement
Weight replacement
Weight per cent Li_2O

FIG. 4.—Relation between gouge resistance and lithia content.

[16] James Bailey, "Scratch-Resisting Power of Glass and Its Measurement," *Jour. Amer. Ceram. Soc.*, **20** [2] 42–52 (1937).

[17] W. N. Harrison, "Tentative Tests for Abrasion Resistance," *Proc. Third Annual Forum, Porcelain Enamel Inst.*, pp. 32–37, October, 1938; *Ceram. Abs.*, **18** [6] 150 (1939).

* The changes in surface-abrasion resistance depicted by these curves differ from those originally stated when this paper was presented. The gloss scale of the reflectometer used in this work was recalibrated at the Bureau of Standards by an improved method, and the abrasion data were corrected on the basis of the new calibration.

[18] R. S. Hunter, "Multipurpose Photoelectric Reflectometer," *Jour. Research Nat. Bur. Standards*, **25** [5] 581–618 (1940); R.P. 1345; *Ceram. Abs.*, **20** [7] 175 (1941).

† Reflectance Test for Opaque White Porcelain Enamels. Porcelain Enamel Institute, March, 1937.

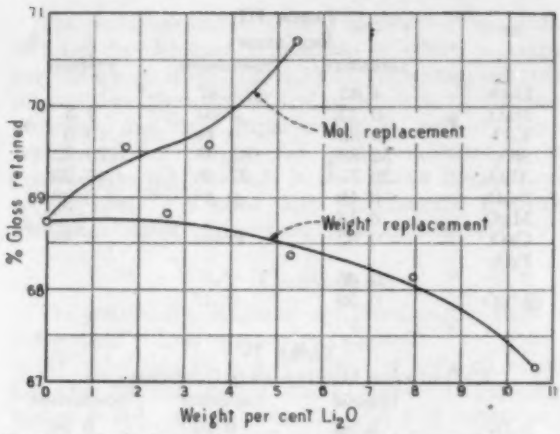

FIG. 5.—Relation between surface abrasion resistance and lithia content.

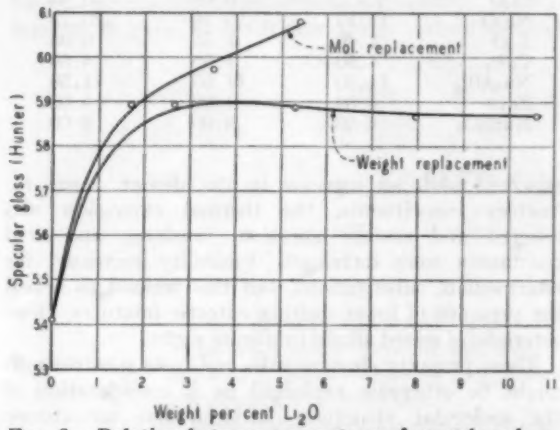

FIG. 6.—Relation between percentage of specular gloss (perfect mirror, 100%) and lithia content.

substitution of lithia for soda on weight basis and increased continuously on mol basis.

(*G*) *Acid Resistance:* The "New South Wales test," now in experimental use in the hollow-ware industry, was used to measure acid resistance. A pan is filled as full as convenient with boiling 0.5% citric acid and allowed to stand 24 hours; the solution is poured off and evaporated, and the weight of the ignited residue is reported as weight of enamel dissolved per square centimeter of surface exposed to action of the acid. Five pans were prepared with each enamel. The pans were bowl-shaped, 26-gauge, 14 cm. in diameter, and 6.5 cm. deep. Enamels were applied at 66 gm. per sq. ft.

The weights of residue were plotted against lithia content in Fig. 9 and showed, with weight replacement, a slight decrease in solubility to about 2.5% of lithia followed by a sharp and continuous increase. With mol replacement, solubility showed an immediate decrease to about 3% of lithia, but no further improvement in acid resistance was noted beyond this point.

(3) Use of Lepidolite and Spodumene

It was not planned, as a part of this study of lithium,

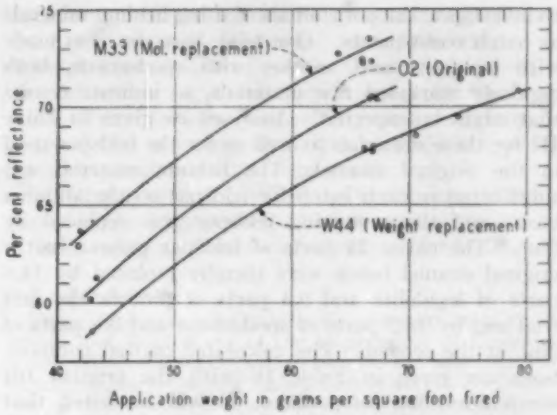

FIG. 7.—Reflectance curves; relation between apparent reflectance (MgO 100%) and enamel application weight for original composition and two extreme replacement compositions.

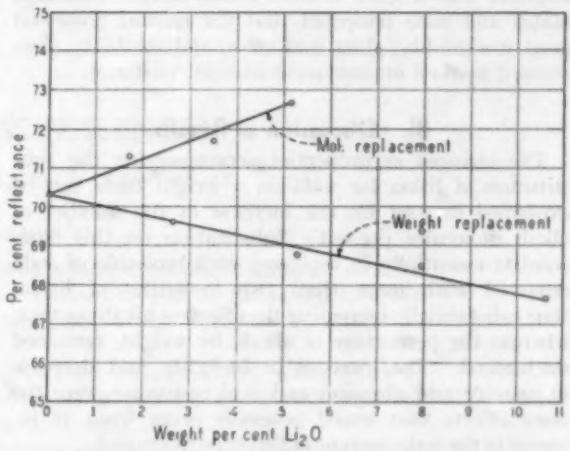

FIG. 8.—Relation between apparent reflectance and lithia content.

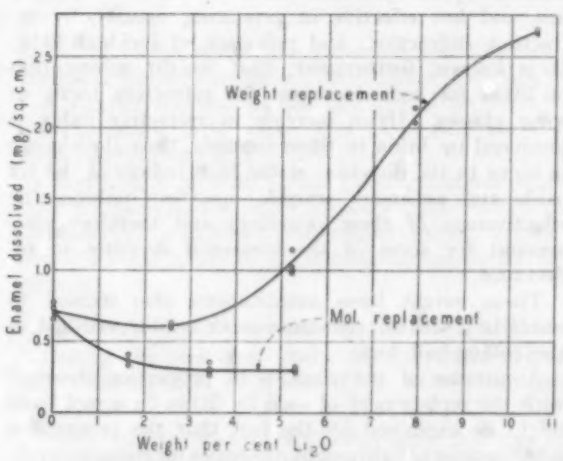

FIG. 9.—Solubility curves, which show relation between enamel dissolved by acid solution and lithia content, depict inversely the acid resistance.

to investigate the possibilities of using lithium minerals as batch constituents. One trial, however, was made with lepidolite and another with spodumene, both regularly marketed raw materials, to indicate results that might be expected. Analyses are given in Table III for these materials as well as for the feldspar used in the original enamel. The lithium material was substituted in each batch for feldspar on the alumina basis, and the remaining feldspar was replaced by flint. The entire 24 parts of feldspar present in the original enamel batch were thereby replaced by 14.6 parts of lepidolite and 9.4 parts of flint in the first trial and by 14.2 parts of spodumene and 9.8 parts of flint in the second. The calculated melted compositions are given in Table IV with the original frit composition for comparison. It will be noted that less than 1% of Li_2O was introduced by these materials.

A 14-kg. batch containing lepidolite produced a frit bearing a pronounced pink color and therefore was not tested. A corresponding spodumene batch, when smelted, was a good white. Some sample enameled plates and pans indicated that the enamel possessed good workability, gloss, and color, and solubility tests showed marked improvement in acid resistance.

TABLE III
ANALYSES

	Lepidolite	Spodumene	Feldspar
Li_2O	4.65	5.87	
NaO_2	0.13	1.03	2.3
K_2O	10.33	0.44	10.0
SiO_2	52.89	62.98	70.72
Al_2O_3	26.77	27.58	16.25
Fe_2O_3	0.19	0.48	0.08
MgO	0.13		
CaO	0.92	Trace	0.43
P_2O_5			
F	3.65		
MnO	0.59	0.37	

TABLE IV
CALCULATED MELTED FRIT COMPOSITIONS

	Original	Lepidolite	Spodumene
B_2O_3	9.96	9.96	9.96
Al_2O_3	3.90	3.9	3.9
SiO_2	44.49	44.65	45.26
Li_2O		0.68	0.85
Na_2O	11.13	10.58	10.73
K_2O	2.40	1.51	0.06
CaF_2	4.50	4.50	4.50
Na_3AlF_6	11.50	11.50	11.50
ZnO	4.00	4.00	4.00
$NaSbO_3$	8.00	8.00	8.00

III. Discussion of Results

The changes in properties accompanying the substitution of lithia for soda on a weight basis can be explained in part by the increase in the number of alkali molecules present. Substitution on this basis consists essentially in replacing each molecule of soda removed with more than two molecules of lithia, thus substantially increasing the effective alkali content, whereas the percentage of alkali, by weight, remained unchanged. The increase in fusibility and decrease in opacity and abrasion and acid resistance were the same effects that would generally occur from an increase in the soda content of this type of enamel.

The greater fluidity of this weight replacement series of enamels possibly permitted ready growth of fluoride crystals, growth to such size that they became less and less effective in producing opacity by refraction, diffraction, and reflection of incident light. It is known, furthermore, that weight substitution of lithia for soda increases the refractive index in some glasses. If an increase in refractive index is produced by lithia in these enamels, then the change in index in the direction of the high indices of the tin oxide and antimony trioxide opacifiers reduces the effectiveness of these opacifiers and therefore may account for some of the measured decrease in reflectance.

These weight basis substitutions also seemed to result in a weaker structure, more readily crushed in the rolling-ball test.

A number of the changes in properties observed with the replacement of soda by lithia on a mol basis might be explained by the fact that the progressive substitutions of lightweight molecules for comparatively heavy ones resulted in lowering the percentage of alkali content with consequent increases in percentages of all other constituents (see Table I). As would be expected with an increase in the denser, more refractory constituents, the thermal expansion was lowered and surface abrasion, crushing, and acid resistances were increased. Fusibility increased for intermediate substitutions, but this seemed to reveal the presence of lower-melting eutectic mixtures, characteristic of mixed alkalis in silicate melts.

These property changes with mol basis substitutions might be otherwise explained by a consideration of the molecular structure. Lithium has an atomic radius of 0.68 a.u. and an ionic potential of 1.5 as compared with an atomic radius of 0.98 a.u. and an ionic potential of 1.0 for sodium. Lithium thus might be expected to promote a tighter, more strongly bonded structure.

There are slight changes in trend at the high lithia ends of the curves in Figs. 1, 4, and 5 and to some extent in Figs. 7, 8, and 9. In making the final substitutions of lithia for soda in both the mol basis and weight basis series, all sodium nitrate was replaced by its Na_2O equivalent of lithium carbonate rather than with lithium nitrate. This was an undesirable substitution, necessitated by a lack of lithium nitrate material. The changes in trend in the figures mentioned might be partly accounted for by the total absence of a nitrate in these end compositions rather than entirely to the high lithia content. When the thermal expansion measurements were made during this investigation, only the end-member compositions were included; the change in thermal expansion with lithia content therefore cannot then be traced. It is reasonable, however, to assume that had the thermal expansion coefficients of the intermediate compositions been determined and plotted against the percentage of lithia, a divergence from the normal trend of the curve might have been noted near the highest lithia composition in each series.

The composition in which spodumene was substituted for feldspar contained, in effect, a higher percentage of silica and a lower percentage of total alkalis than the original frit as a result of the substitution, and some improvement in acid resistance was therefore to be expected. Only one batch of this composition was smelted, however, and it could not be decisively concluded that the observed improvement was caused solely by the use of spodumene.

IV. Conclusions

The following conclusions are given on the basis of the general enamel composition studied:

(1) The substitution of lithia for soda on a mol basis results in improved fusibility, gloss, and opacity; higher gouge, surface abrasion, and acid resistances; and lower thermal expansion coefficient.

(2) When lithia is used to replace soda on a weight basis, the enamels show increased fusibility; a small increase in gloss; a small decrease in surface abrasion resistance; marked decreases in opacity, gouge resistance, and acid resistance; and little change in thermal expansion coefficient; there is, however, a noticeable lowering of the transformation temperature.

(3) From the relative fusibility curves, it may be deduced that one part by weight of lithia is approximately equivalent to 2.3 parts of soda.

(4) Trials with lepidolite and spodumene indicate that certain improvements in properties might be expected when spodumene is substituted for feldspar.

Acknowledgment

The author wishes to express his appreciation to G. H. Brown and L. E. Kane of the Department of Ceramics, Rutgers University, for making possible this investigation; he also wishes to thank P. C. McCollom and R. R. Danielson of the Metal & Thermit Corporation and W. N. Harrison and L. Shartsis of the National Bureau of Standards for their helpful advice and for the use of laboratory facilities during parts of this investigation.

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SEALED GLASS BUSHINGS*

By W. W. Grigorieff and C. M. Lampman, Jr.

Abstract

Glass bushings with sealed-in metal inserts have been developed to fulfill the need for hermetically sealed electrical apparatus. A special lead-borosilicate glass called GE 1075 and a 42% nickel-iron alloy, both of which have like thermal expansion characteristics, will produce a matched seal.

The forming operation consists of melting the glass electrolytically, casting into preheated molds of graphite or iron which have the metal inserts in place, annealing from 500° to 350°C., and cutting off the stub end of the bushing.

The finished bushings are fastened to the apparatus by welding or soldering, which eliminates the use of gaskets.

A detailed description of the construction, forming process, and testing procedure is given.

I. Introduction

The need for hermetically sealed insulating bushings became evident with the advent of liquid- and gas-filled electrical apparatus operated under pressure. The function of a bushing is to carry a lead from the interior of a piece of apparatus to some point outside the shell where contact can be made. Such function prescribes that it must be (1) an adequate insulator, (2) pressure tight against liquids and gases, (3) mechanically strong, (4) weather resistant, (5) capable of withstanding sudden temperature changes without rupturing, and (6) easily fastened to apparatus by welding or soldering.

One method of producing a sealed bushing is to use a solder joint between a previously metallized porcelain or glass surface and the required metal shapes. Another method is to use glass in place of solder to join the porcelain to the metal, the glass and metal having a thermal expansion coefficient near that of porcelain.[1]

A simpler solution to the problem of producing a sealed bushing is to make it of glass with sealed-in metal inserts that can later be attached to the apparatus by soldering or welding.[2] The glass and metal inserts have comparable thermal expansion coefficient curves and thus give a matched glass-to-metal seal. Figure 1 shows several types of glass bushings made by this method.

II. History and Properties of the Matched Seal

During the past few years, several metal-to-glass seal combinations of matched or nearly matched

* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 21, 1942 (Glass Division). Received October 5, 1942.

[1] W. E. Bahles, "New Type Vacuum Seal," *Elec. Eng.*, **57** [7] 373–78 (1938).

[2] A. W. Hull, R. W. Moore, and O. H. Doll, "Sealed Glass Bushings for Electrical Apparatus," *Gen. Elec. Rev.*, **42** [12] 525–28 (1939); *Ceram. Abs.*, **19** [3] 64 (1940).

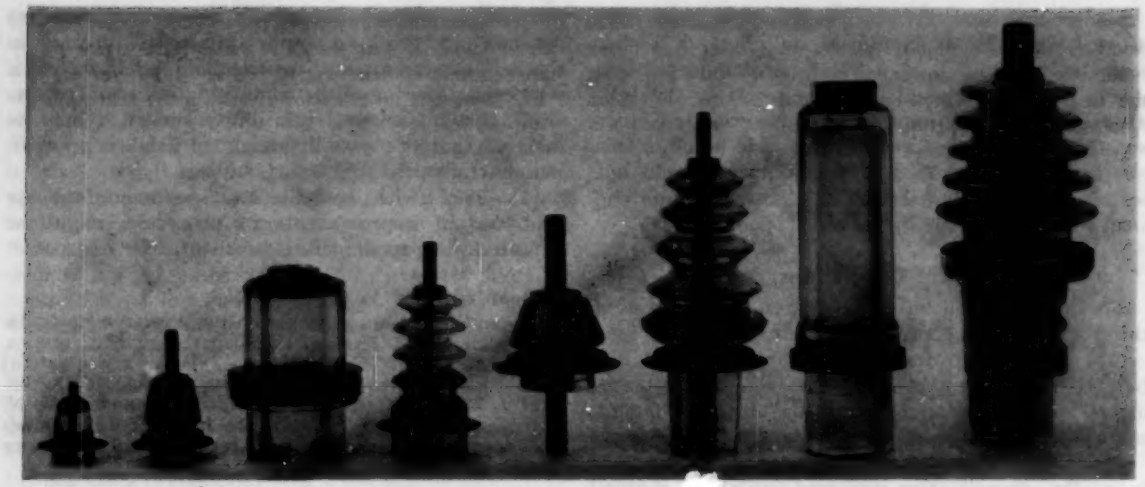

FIG. 1.—Several types of metal-to-glass sealed bushings for electrical apparatus.

thermal expansion coefficients have been developed for sealing the leads of vacuum tubes. These have been fully described elsewhere,[3] and a brief summary is given here.

Four metal-to-glass combinations are listed in Table I, and Figs. 2 and 3 show contraction curves for two of these. Of the combinations listed, the Fernico-Corning 705 AO (Fig. 2) gives a good seal, but the composition of the Fernico must be kept within exact limits and it is not easily adapted to forming operations. The chrome iron-LN 286 and the iron-LN 542 combinations also form good seals, but their high coefficient of expansion reduces their ability to withstand thermal shock. The nickel steel-GE 1075 combination (Fig. 3) appears to have the greatest number of desirable properties for making sealed bushings; the expansion coefficient is low, the metal is more resistant to oxidation than iron, and it can be readily shaped.

The composition and properties of GE 1075 glass are as follows: SiO_2 34, Al_2O_3 7, B_2O_3 27, PbO 30, and Na_2O 2%; average coefficient of expansion (0° to 300°C.) is 5.5 × 10^{-6}; softening point, 590°C., and sealing point with 42% nickel-steel alloy, 450°C. It is essentially a glass of the lead-borosilicate type.

III. Construction of Sealed Bushing

Although the sizes and shapes of the bushing vary widely, a single basic construction is followed in every case. Figure 4 shows a sectional diagram of two types of bushings. Each bushing requires two metal inserts; one is a small cuplike cap whose edge enters the glass at the top of the bushing, and the other is a flange which encircles the bushing near the bottom where its edge enters the glass. The depth of penetration of these parts is from 1/8 to 3/8 in. according to the size of the bushing. The cap is brazed either to a short copper stud (Fig. 4(1)), to which a cable can be brought through a hole in the center of the glass shape, or to a central conductor (Fig. 4(2)). Other parts of the construction as shown in Fig. 4 are (1) a dummy-cap which keeps the glass from contacting the braze joint or copper stud; (2) an idler ring which prevents the

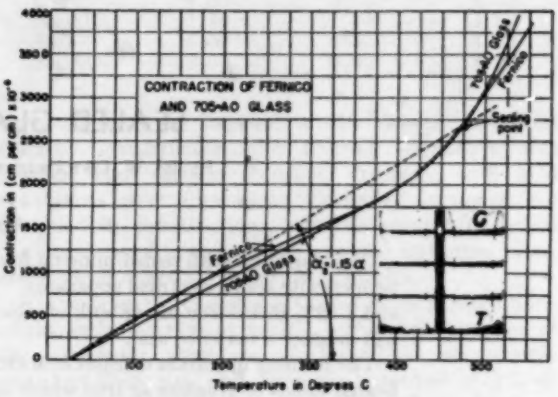

FIG. 2.—Thermal contraction of Fernico and 705-AO glass; insert shows stress pattern of test seal between these materials.

TABLE I

GLASS-TO-METAL SEAL COMBINATIONS

Metal name	Metal composition	Matching glasses	Avg. coeff. of expansion × 10^{-6} (0°–300°C.)
Fernico	54 Fe, 31 Ni, 15 Co	Corning 705 AO	4.95
Chrome iron	26 Cr, 74 Fe	LN 286	10.1
Iron	Fe	LN 542	12.8
Nickel-Steel (B7Y13A)*	42 Ni, 58 Fe	GE 1075	5.5

* General Electric Co. designation.

[3] (*a*) A. W. Hull and E. E. Burger, "Glass-to-Metal Seals," *Physics*, **5** [12] 384–405 (1934); *Ceram. Abs.*, **14** [6] 136 (1935).
(*b*) A. W. Hull, E. E. Burger, and L. Navias, "Glass-to-Metal Seals, II," *Jour. Applied Physics*, **12** [9] 698–707 (1941); *Ceram. Abs.*, **21** [1] 8 (1942).

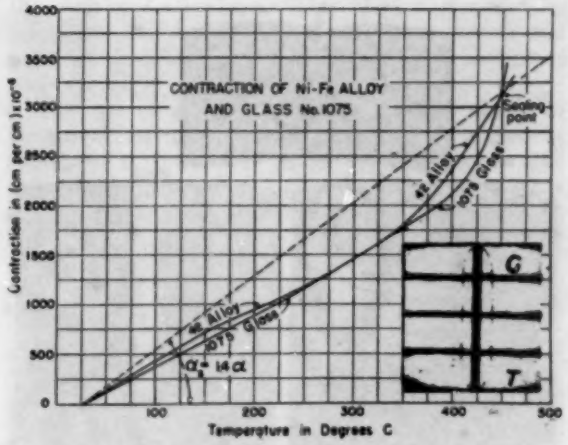

FIG. 3.—Thermal expansion curves of No. 42 alloy and 1075 glass and photoelastic stress pattern of seal between them; absence of stress in seal is shown by straightness of interference lines crossing it.

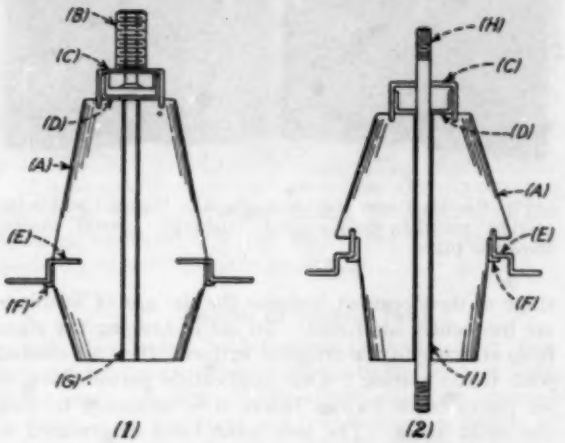

FIG. 4.—Construction of two metal-to-glass sealed bushings; *A*, glass body; *B*, copper stud; *C*, cap; *D*, dummy cap; *E*, flange; *F*, idler ring; *G*, tube; *H*, central conductor; and *I*, protecting sheath.

glass from touching the flange except where the seal is made; and (3) a sheath of alloy around the central conductor to prohibit the glass from sticking to the copper, which has a much higher expansion coefficient. Thus the only metal that the glass comes in contact with is the matching alloy.

Another important feature of the construction is a thin coating of lead-free glass on the surfaces of the inserts where the seal is made.[4] The reason for this is that the nickel-steel alloy will plate out lead from the GE 1075 glass if direct contact is made during the forming process. This lead layer at the interface tends to produce a weak seal. Inasmuch as a thin layer of precoating glass does not appear to affect the matching properties of the main glass or the metal, its coefficient of expansion need not match that of the molded glass

[4] Louis Navias (General Electric Co.), "Glass-to-Metal Seal," U. S. 2,193,640, March 12, 1940; *Ceram. Abs.*, 19 [5] 113 (1940).

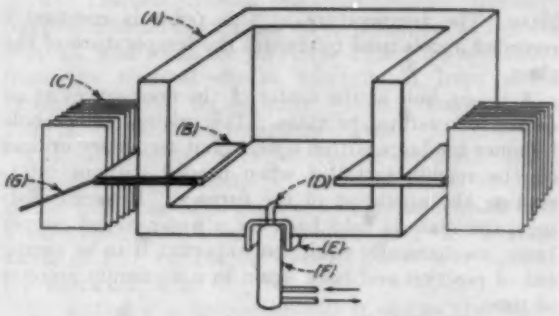

FIG. 5.—Construction of electric furnace for melting and casting GE 1075 glass; *A*, furnace lining: *B*, copper electrode; *C*, cooling fins; *D*, primary office; *E*, secondary office; *F*, water-cooled stopper; and *G*, thermocouple.

but should be such that the glass will adhere to the metal. Corning 705 AO sealing glass is used for this purpose at the present time.

When it is desirable to have a hole through the body of the glass to allow a cable to be brought to the stud, it is accomplished in one of two ways. If the diameter of the hole is in the range of $^1/_8$ to $^1/_4$ in., a small tube of the nickel-steel alloy is supported in the mold by a tungsten pin. The pin is withdrawn after the bushing is formed, leaving a small metal-lined hole. For holes of larger diameter, a steel pin coated with flint is supported vertically in the mold. As in the first case, the pin can be readily withdrawn after the bushing is completed.

IV. Method of Manufacture

(1) Glass Raw Materials

Raw materials of U.S.P. quality are used for the glass at the present time. This does not preclude the possibility of using commercial materials but minimizes control of glass composition at this stage of the development.

After they have been weighed, the materials are thoroughly mixed and then calcined at 450°C. for an hour. A large portion of the gases may be removed by this process before the batch is introduced to the melting furnace, thereby speeding up the time of melting and fining.

(2) Melting Furnace

The glass is melted electrolytically in a small furnace of 100-lb. capacity (Fig. 5). It consists of a refractory shell, 18 in. long, 9 in. wide, and 15 in. deep on the inside. At each end, $2^1/_2$ in. from the floor, a flat copper electrode extends a distance of $3^1/_2$ in. into the chamber. On the ends of the electrodes exposed to the air, thin copper fins serve to keep the temperature of the electrode below its melting point. Radiation of heat by the fins is quickened by a stream of low-pressure air.

For placing a thermocouple, one electrode is provided with a small hole at its center which extends parallel with the flat surfaces to within $^1/_2$ in. of the end in the

glass. The temperature at this point is constantly recorded and is used to control the temperature of the glass.

A $^5/_{16}$-in. hole at the center of the floor serves as an orifice for casting the glass. The original orifice hole becomes too large within a week, but secondary orifices can be readily installed when needed without interrupting the operation of the furnace. Between castings, the glass is held back by a water-cooled copper bung, mechanically equipped to permit it to be swung out of position and back again in a minimum amount of time.

(3) Operation of Furnace

During the normal operation of the furnace, 12 kw. of power are used to melt the glass and to maintain a temperature of 1250°C. at the electrode level.

The glass temperature varies directly with the current supplied, which in turn is dependent on the applied voltage. The control, therefore, consists of a variable voltage regulator having a range of 0 to 1500 volts. The GE 1075 glass is usually held at 300 volts and 40 amperes, but this volt-ampere relationship is not the same for the other glasses listed in Table I.

To start the furnace, enough cullet to cover the electrodes is added and brought to a molten state by gas burners. Fifteen hundred volts are applied, and within one or two minutes some current begins to flow. The burners are removed, calcined material is added, and the controls are regulated until stability is reached.

Of the 100 lb. of glass in the furnace, about 60 lb. can be used in any one day, inasmuch as the glass level must always be held above the electrodes. After casting, enough calcined material is added to bring the load back to 100 lb. The new charge is sufficiently melted and refined within 24 hours.

The average life of a furnace is about ten weeks of continuous operation, but it can easily be torn down and rebuilt in one day. The greatest erosion of the lining occurs at the electrode level where it causes the inside of the furnace to assume a somewhat elliptic shape.

(4) Metal Parts Preparation

The seal areas of the cap and flange are lightly sandblasted and sprayed with powdered Corning 705 AO sealing glass suspended in alcohol. The glass is fused on by firing the pieces in an enameling furnace at 900°C.

The enameled cap is fastened to the stud with a low-melting (650°C.) silver solder. The heat necessary for the braze is obtained by applying a torch to the stud only, thus protecting the enameled surface of the cap from damage by the open flame.

(5) Forming and Annealing

The bushings are formed by casting the glass into graphite or iron molds which have been previously supplied with metal inserts. The molds are split on the vertical center to remove the bushings. Figure 6 shows some of the molds with the inserts in place. Although their life is short compared to iron, graphite molds are relatively inexpensive to form and can be quickly machined. Thus they are preferable at this stage of development because the designs of bushings are frequently improved. To aid in keeping the glass from sticking to the graphite surfaces, they are dusted with boron nitride.[5] One application permits five or six pieces to be formed before it is necessary to dust the mold again. The iron mold faces are treated in the usual manner.

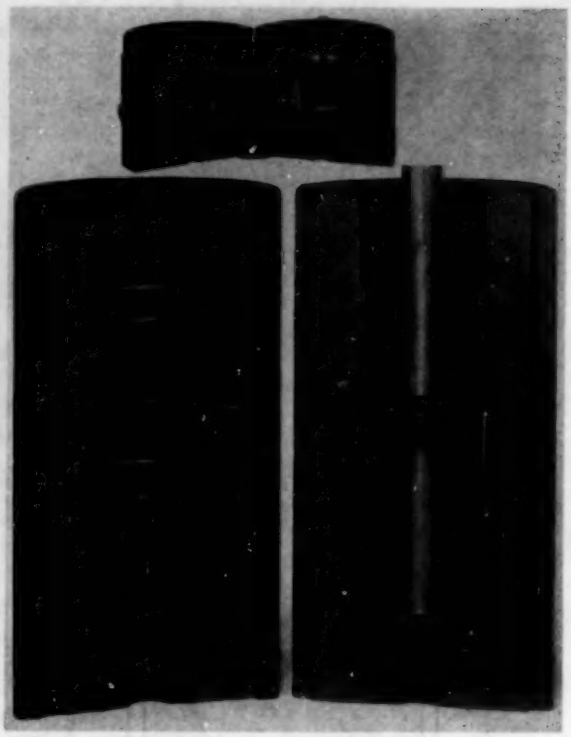

FIG. 6.—Cast-iron (*top*) and graphite (*bottom*) molds for casting metal-to-glass sealed bushings; metal inserts shown in place.

Before using a mold, the metal inserts are put into place, the mold is clamped together, and the whole unit is preheated to 400°C. The glass is then tapped, and the mold is held by suitable handles or it is spun on a turntable under the stream of glass until it is full. Bushings up to 6 in. high are removed from the molds and placed in the annealer on racks as soon as they have cooled to a point where they will hold their shape. More inserts are then put into the mold, the preheating process is repeated, and the following bushings are made. Larger bushings are placed directly into the annealer as soon as the mold is filled, and they remain in the mold until the annealing is completed.

The annealing cycle for the smaller bushings consists of cooling from 500° to 350°C. in 12 hours, whereas 24 hours are required for large bushings to cool through the same temperature range.

(6) Finishing and Testing

Each bushing has a stub end of excess glass, which is

[5] R. W. Moore (General Electric Co.), "Glass Fabrication Process and Mold," U. S. 2,201,049, May 14, 1940; *Ceram. Abs.*, **19** [7] 162 (1940).

the shrinkage allowance. This piece is removed by rotating the bushing on its vertical axis in a lathe and using a silicon carbide cut-off wheel for the cutting as shown in Fig. 7.

A torque, ranging from 10 to 40 ft.-lb. according to the size of the unit, is applied to the stud to assure the soundness of the brazed joint. The bushing is then subjected to 40 lb. per sq. in. of air pressure while submerged in water, the pressure being sustained for a 15-minute period. During that time, it is critically inspected for possible leaks.

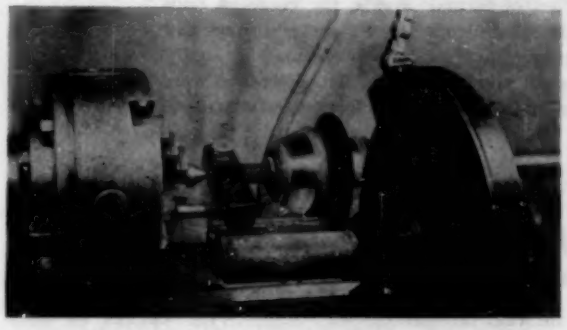

FIG. 7.—Glass bushing in place for removal of shrinkage end by cut-off wheel; water lubrication not shown.

A light sandblast on the exposed metal parts removes the oxide that has formed during the making of the bushing and prepares the surface of the flange for soldering or welding to the apparatus.

V. Results of Special Tests

(*A*) *Weathering:* Sealed glass bushings have now been in service on outdoor applications for more than three years. A slight dulling of the glass has occurred in some cases, but there has been no sign of failure or leakage.

Some samples have been subjected for a year to the following accelerated weathering test: (*a*) raised from room temperature to 55°C. by steam (5 hours); (*b*) held at 55°C., 100% of humidity for 6 hours; (*c*) raised to 75°C. by hot air; (*d*) held at 75°C., 100% of humidity for 6 hours; and (*e*) steam and hot air turned off and outside atmosphere introduced until 25°C. is reached (4 hours). This cycle is repeated every 24 hours.

These samples also showed a slight dulling of the glass and rusting of the metal parts, but they were still tight under 40 lb. per sq. in. of air pressure.

(*B*) *Thermal Shock Resistance:* Sealed bushings have been found tight under 40 lb. per sq. in. at 140°C., −50°C., and room temperature. They did not suffer from the thermal shocks encountered from either extreme to room temperature. Direct removal from 140° to −50°C. did not rupture the seal.

(*C*) *Mechanical Strength:* Tensile strength tests, accomplished by sealing two pieces of nickel steel together with a layer of glass and applying tension with a standard steel-testing machine, gave an average value of 2.27 kg. per sq. mm. (3175 lb. per sq. in.) for tensile strength.[3(b)]

By applying a torque of 110 ft.-lb. to the $^{3}/_{4}$-in. central conductor of one type of bushing, it was possible to twist off the copper conductor without damaging the glass or the seal.

(*D*) *Electrical Characteristics:* All of the bushing designs have been tested for wet and dry flashover. The results in every case are much higher than the rating of the bushing when it is in service; for example, a bushing rated at 15 kv., which has a creepage length of $10^{1}/_{8}$ in. and a strike distance of $6^{3}/_{4}$ in., gave the following results:

Dry flashover, standard conditions: minimum 86.5 kv.; average, 89.0 kv.; maximum, 90.2 kv.
Wet flashover, bushings vertical: 55–62 kv.; inclined 15°, 53–56 kv.
Impulse flashover, standard conditions and $1\text{–}^{1}/_{2}\text{–}40$ negative wave: 178 kv.

VI. Summary

Cast glass bushings with sealed-in metal inserts are successfully answering the need for hermetically sealed electrical apparatus. This development is based on the use of metal-glass combinations of matched thermal characteristics, and it has resulted in the sealing of heavy metal pieces in large masses of glass.

The availability of gas, oil, and vacuum-tight, lead-in bushings has presented new possibilities to the designing engineer and has resulted in electrical apparatus of greater efficiency and longer life.

Acknowledgment

The authors wish to acknowledge their indebtedness to A. McK. Gifford and V. E. Goodwin, who have guided this work, as well as to G. H. Porter, O. H. Doll, and many others of their colleagues, who have contributed to the success of this investigation. This development was begun in the General Electric Research Laboratories at Schenectady, N. Y., by A. W. Hull and collaborators, to whom grateful acknowledgment is also made.

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COLLOID CHEMISTRY IN CERAMICS *

By A. L. Johnson

Abstract

The advancement of ceramics from an art to a science, a transition which has been in progress for the last forty odd years, parallels the development of the science of colloids. Whereas the application of the fundamentals of the physical and the chemical sciences has indicated to the ceramic engineer the methods to be used in solving his problems, it has been in the interpretation of these researches that the colloid science has contributed more than was ever anticipated. For a more practical knowledge of the basic principles involved in the fabrication of ceramic goods, the ceramist finds that a thorough understanding of the colloid-physical concept of clays and other raw materials supplies him with the answers to many of his industrial problems.

The subject matter of ceramics or, more specifically, the fabrication of ceramic ware is discussed from the colloid-physical standpoint in an effort to illustrate what colloid chemistry means to the ceramic industry.

I. Introduction

Some time during the Stone Age, the Neolithic man found that when an earthy substance, which is now called clay,† was tempered with water the mass could be readily formed into any desired shape and this shape was retained when the forming pressure was released. Those first pieces of handmade pottery represent the birth of the ceramic industry and make it one of the oldest industries still in existence.

Progress, which develops any industry, made its appearance early. Among the first improvements was the potters' wheel, which was in activity in all the great nations of antiquity during 1500 to 900 B.C. The use of heat to impart durability to ceramic ware was soon incorporated into the fabricating process; the decoration by means of glazes, colors, or stains rose to its height as evidenced by the work of the Chinese from the year A.D. 20. These developments, and many others similar in nature, contributed to the advancement of the art of ceramics. During the nineteenth century, however, at about the time that it was recognized that matter existing in a colloidal state did not necessarily comply with the physicochemical laws, the art of ceramics began its transition from an art to a science.

Inasmuch as the principal raw material of the ceramic industry is clay and since this material exists in a finely divided or colloidal form, it follows that a knowledge of the colloidal behavior of clay would supply the ceramic engineer with information with which he could go about fabricating ware on a commercial scale. Some of the important colloidal properties of clays, which are the basis for the various methods of fabricating ceramic goods in mass production, are discussed here.

II. Clay as a Raw Material

Because of their scientific interest, clays have been the object of intensive study for many years. As a result of these studies, it is generally accepted that twelve distinct minerals belonging to one of four groups make up the family of clay minerals.[1] The kaolin group which is of the greatest importance to the ceramist contains at least five minerals. Of these five, the mineral kaolinite, $Al_4(Si_4O_{10})(OH)_8$, occurs in such abundance as to be industrially worthwhile. The ceramic engineer therefore contents himself with only one member of the clay-mineral family, and, chemically speaking, this one mineral should cause little difficulty.

Table I gives the chemical (ultimate) analysis of two samples of clay obtainable from areas of the United States which produce the major output of ceramic clays. Although there is a significant difference in the percentage of Al_2O_3 and K_2O between the samples, the rational analysis would probably show sample No. 1 to contain orthoclase (potash feldspar) present as an admixture, which would account for the greater K_2O content. The lower Al_2O_3 content of sample No. 1 could be accounted for by the presence of less kaolinite and some free silica as sand. The presence of organic material points to the high loss of ignition on clay No. 1. The physical properties of the two clays vary somewhat as shown in Table I.

This variation is not an isolated case. To the ceramic engineer, the difference between the two clays would be apparent immediately, not from the chemical analysis but by noting the physical properties of each clay. Rarely does he use a chemical analysis to account for differences in physical properties for no satisfactory correlation between chemical analysis and raw physical properties has yet been worked out. Sample No. 1 would be termed a ball clay, whereas No. 2 is a kaolin or china clay. These terms have been adopted

* Presented at the Fall Meeting, American Chemical Society, Colloid Division, September 7–11, 1942, Buffalo, N. Y. Received October 22, 1942.

† The term clay used in this paper refers to the natural occurring material consisting chiefly of the mineral, kaolinite, $Al_4(Si_4O_{10})(OH)_8$.

[1] (*a*) Linus Pauling, Nature of Chemical Bond and Structure of Molecules and Crystals. Cornell University Press, Ithaca, New York, 1940.

(*b*) E. A. Hauser, "Colloid Chemistry in Ceramics," *Jour. Amer. Ceram. Soc.*, **24** [6] 179–89 (1941).

(*c*) R. E. Grim, "Modern Concepts of Clay Minerals," *Jour. Geol.*, **50** [3] 225–75 (1942); *Ceram. Abs.*, **21** [8] 177 (1942).

(*d*) P. F. Kerr, "A Decade of Research on Nature of Clay," *Jour. Amer. Ceram. Soc.*, **21** [8] 267–86 (1938).

TABLE I

CHEMICAL ANALYSIS OF TWO CLAY SAMPLES

	Chemical analysis (%)		Theoretical analysis (%)
	Clay No. 1	Clay No. 2	
SiO_2	44.2	44.7	46.5
Al_2O_3	31.6	38.6	39.4
Fe_2O_3	1.1	0.9	
TiO_2	0.8	0.5	
CaO	0.9	0.2	
MgO	0.3	0.3	
Na_2O	0.1	0.1	
K_2O	1.1	0.1	
Loss	19.6	13.8	14.0
	Rational analysis (%)		
Clay	80	98	100
Quartz	3	0	0
Feldspar	6	1	0
	Physical properties		
Dry strength	1000	125	
Vol. shrinkage (%)	30	10	

to depict clays with distinct properties, and yet, when carefully analyzed chemically, the results will show only slight differences in chemical analysis as illustrated in Table I. X-ray studies will reveal that the mineral present is substantially kaolinite. By more sensitive tests, such as differential thermal analyses,[2] small quantities of quartz or the other clay minerals may be detected. The ceramist, however, has needed more positive information; because of their shortcomings, therefore, these techniques regularly used in most chemical industries had to be replaced by a cut-and-try type of investigation. Even today, the most widely used method of selecting clays for industrial use is a tedious measurement of physical properties. The clays are made into test specimens by tempering with water and forming, followed by the long period of measuring five to ten physical properties in order to determine the commercial possibilities of any clay. The results often indicate the clay to be unsuitable for use because of some deficiency in its physical properties although, economically, it may be advantageous to use the material. The ceramic engineer, however, has no choice but to shop around until he locates a clay which possesses the desired properties even though the economics of the situation favor a clay nearer his plant.

The term "colloidal" has been associated with clays for many years, but some time during the nineteenth century they were given a closer colloidal study. As a result of this examination, certain properties of clays were directly assigned to their colloidal nature, and gradations in these properties were attributed to variations in the amount of colloidal material present; for example, today the particle-size distribution[3] of clays can be measured. Figure 1 shows the type of data obtained on samples represented by the analyses given

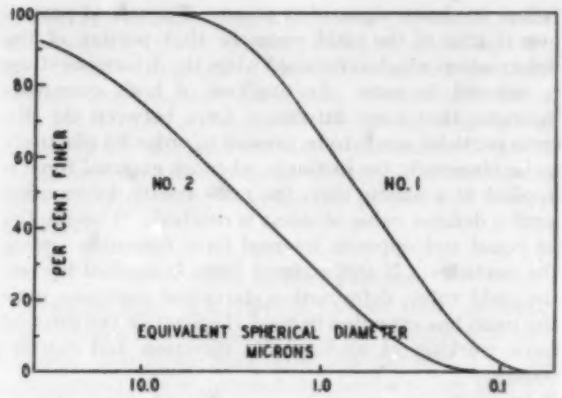

FIG. 1.—Particle size distribution on two typical ceramic clays.

in Table I; clay No. 1 is shown to be considerably finer than clay No. 2. If the exchange capacity* of each clay were determined in addition to the particle size distribution, differences would be found which also could be correlated with the physical behavior of the samples. This was a beginning. Colloidal chemistry revealed significant differences not shown by any other method of analysis. As a result of a program of research on clays which has been in operation for several years, certain variables are now known to control the physical properties of clay, namely, (*a*) surface area, (*b*) particle shape, and (*c*) the electrokinetic state of the colloidal micelle. It is logical to assume therefore that given any two samples of the same clay mineral whose surface area, particle shape, and electrokinetic state are identical would display the same physical properties no matter what their origin. Such a statement would never have been made twenty years ago, and yet experimental evidence to support this statement may soon be available.

The properties of clays, which are of greatest interest from a colloid-physico standpoint, will be discussed in the next sections.

III. Plasticity of Clays

No single property of clay is as important as that of plasticity. Without it the potter could not mold clay into the desired shape nor would the jigger tool make a permanent impression.

Plasticity is defined as the ability of a body to retain part or all of its deformation after the deforming stress is reduced to zero.[4] A measurement of plasticity is difficult to obtain because two parameters define the system. The first is known as extensibility and refers to the amount of extension a plastic mass will undergo

[2] F. H. Norton, "Critical Study of Differential Thermal Method for Identification of Clay Minerals," *Jour. Amer. Ceram. Soc.*, **22** [2] 54–63 (1939).

[3] (*a*) E. A. Hauser and C. E. Reed, "Development of New Method for Measuring Particle-Size Distribution in Colloidal Systems," *Jour. Phys. Chem.*, **40** [9] 1169 (1936); *Ceram. Abs.*, **20** [5] 128 (1941).

(*b*) F. H. Norton and S. Speil, "Measurement of Particle Sizes in Clays," *Jour. Amer. Ceram. Soc.*, **21** [3] 89–97 (1938).

* The exchange capacity of a clay is the amount of ions which can be replaced in the sample, usually reported in milliequivalents per 100 gm. of sample.

[4] E. A. Hauser and A. L. Johnson, "Plasticity of Clays," *Jour. Amer. Ceram. Soc.*, **25** [9] 223–27 (1942).

before it shows signs of rupture. The second parameter is that of the yield value or that portion of the deformation which is retained when the deforming stress is reduced to zero. An analysis of both quantities indicates that some attraction force between the discrete particles needs to be present in order for plasticity to be observed; for instance, when an external force is applied to a plastic clay, the mass resists deformation until a definite value of stress is reached. This implies an equal and opposite internal force operating among the particles. If the external force is applied beyond the yield value, deformation starts and continues until the mass has extended beyond the limit of the internal force working in an opposite direction and rupture occurs.

Many theories as to the nature of this internal force associated with the particles have been proposed. The colloidal theory,[4] based on modern interpretations of the micelle, seems to give the most plausible explanation and furthermore supplies the ceramist with information that is of considerable importance when a manipulation of the property is necessary. Plasticity from the colloidal standpoint will therefore be considered here.

The forces of attraction associated with a colloidal micelle of clay arise from the following sources[4]: Certain areas of the crystalline fragment have broken valence bonds which are unsaturated and capable of preferentially adsorbing certain ions, usually the hydroxyl ion; the particle thus acquires a net negative surface charge. Attraction forces also are set up between the now negatively charged clay particle and any positive charges in the vicinity. The repulsion forces associated with this micelle originate because of the counterions which swarm about the colloidal particle in an effort to neutralize its surface charge. These counterions complete the diffuse double layer; and although they may be any cation, the magnitude of the repulsive force existing in the system varies, depending on the type of cation which serves as the counterion. When hydrogen serves as the counterion, the repulsion force existing in the system is small enough that the attraction forces completely nullify the repulsion force, and the net result is an attraction force of some magnitude. Figure 2 shows this result clearly. The negative signs represent the preferentially adsorbed hydroxyl ions. Curve *A* gives the relation of the overall attraction forces in the system as a function of the distance from the particle. The hydrogen counterions are represented by the positive signs. Because of their size, hydration, and equilibrium distance, these ions can enter the water hull (represented by the dotted line) and situate themselves close to the adsorbed hydroxyl ions in an effort to form an electrically neutral system. Curve *R* represents the overall repulsion force of the system as a function of the distance from the particle.

Inasmuch as the lyosphere is an inherent part of the colloidal particle, the type and magnitude of the force existing at this point have an enormous effect on the properties of any clay–water system. According to Fig. 2, the resultant force at the edge of the water hull

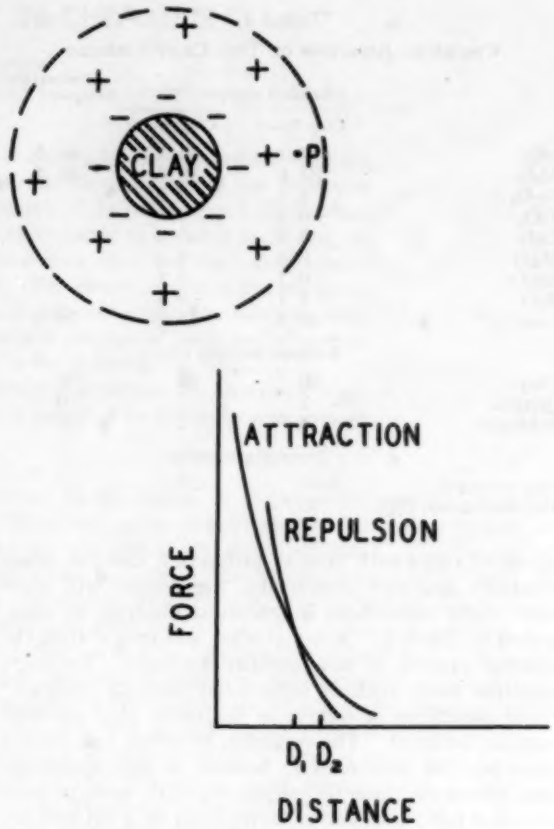

FIG. 2.—Schematic representation of the coulombic forces associated with hydrogen clay.

(represented by d_2) is a force of attraction. Hydrogen counterions will cause an attraction force of the greatest magnitude to be present at this point, and according to the lyotropic series, trivalent and divalent ions decrease this value until finally the monovalent sodium and lithium ions cause a repulsion force of considerable magnitude. Figure 3 shows the arrangement of ions associated with the clay micelle and the relation of the forces present when sodium ions serve as the countercharges. The medium in this case is alkaline for it is impossible to have sodium as counterions without the presence of an excess in the medium. In this case, because of the hydration size and equilibrium distance of the sodium ions, point *P*, where the charge associated with the colloidal micelle approaches zero, will be some distance from the particle, and the average distance from the particle at which all the ions (the counterions) of the diffuse double layer may be considered to act is somewhere in the vicinity of the edge of the water hull. The resultant force at point d_2, therefore, is a force of repulsion (see Fig. 3).

In a clay–water system whose plasticity is of interest, the type and magnitude of the resultant force at the lyosphere are important. If the resultant force is one of repulsion between micellae and therefore between particles and if an external force is applied, deformation and rupture of the clay mass would be expected to

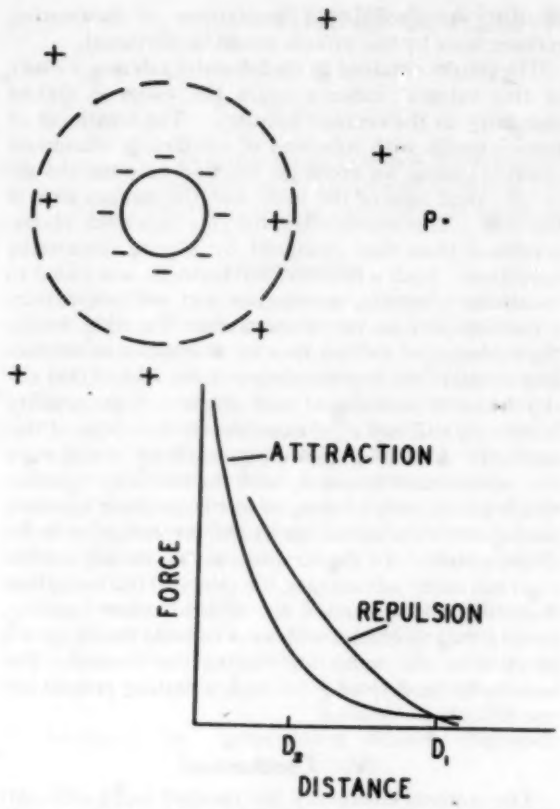

FIG. 3.—Schematic representation of the coulombic forces associated with sodium clay.

occur more readily and with the expenditure of a weaker force. Such a system would be considerably less plastic than one that contained clay particles in which attraction forces were present at the edge of the lyosphere because, in this instance, an external force of greater magnitude would be needed to deform the mass and finally to cause rupture. By this hypothesis, a clay containing sodium in the exchange positions or as counterions would be the least plastic, and a gradation in this property could be expected in the progression from sodium to hydrogen in the Hofmeister series. This observation agrees with experimental data, and it is a justification of the interpretation of plasticity from a colloid-physico standpoint.

The theory tells the ceramist in practical terms that the most economical way in which he can manipulate the plasticity of a given clay is to substitute the counterions for trivalent aluminum or monovalent hydrogen ions. The treatment may cost ten or twenty cents per ton of clay.

Until recently, the property of plasticity has been observed only among the clay minerals. Even then a certain optimum size of particle is required below which this property is present. For kaolinite, an equivalent spherical diameter of about four microns[5] or less is required before plasticity manifests itself. This property can be controlled and regulated for clays because the correlation of the electrokinetic state of the particle and plasticity has been theoretically determined. It does not seem far-fetched to believe that some day the so-called nonplastic minerals will exhibit plastic properties[6] as soon as the proper electrokinetic state has been determined for this property to become apparent.

IV. The Casting Process

Ceramic ware is fabricated by two main processes which depend on the property of the plasticity of clay, namely, plastic forming and slip forming. In the first method, the water content may be so low that the resulting clay-water mixture is in the form of an almost dry powder, or the water content may be high enough that a plastic doughy mass results. Intermediate water contents are also used and fall under the heading of plastic-forming methods. The slip-forming method, however, is more important from a colloidal viewpoint, and this method of fabricating ware is discussed herein.

For the casting process, the compounded clay mixture is made into a slurry or slip with water. In the earliest days of this process, low specific gravity slips were used in conjunction with plaster of Paris molds. The slip was poured or scooped into the mold and allowed to contact the porous surface until sufficient water was absorbed leaving a leather-hard layer of clay adjacent to the mold. This shell of partially dried clay, which had the exact form of the mold, would finally shrink away and, thus freed, could be removed. At least midway through the 19th century, certain basic salts were used in conjunction with casting slips. It was common knowledge by 1900 that the use of these basic salts permitted the preparation of casting slips with a higher concentration of solids, and it is not uncommon today to find casting slips containing the same amount of water as that used by the plastic-forming process. The addition of 0.1 to 0.3% of the proper deflocculating agents (usually sodium silicate and/or carbonate), however, produces a system of high fluidity, whereas in the absence of these reagents, the clay-water mass would be so stiff that pouring would be impossible.

The importance of a high specific gravity slip for casting is readily seen. In the first place, if clayware casting is carried out by a mechanical dewatering of the slip, less time will be required for the mold to remove sufficient water, causing the clay to set and become rigid. Shrinkage of clay, furthermore, bears a relation to the water content, and the use of high specific gravity slips therefore reduces shrinkage problems correspondingly. Because the deflocculation of the clay particles in a clay–water system lends itself to the production of slips with higher percentages of solids and high mobility, the deflocculation of clay will be considered in some detail.

[5] H. Whittaker, "Effect of Particle Size on Plasticity of Kaolinite," *Jour. Amer. Ceram. Soc.*, **22** [1] 16–23 (1939).

[6] E. O. Wilson, "Plasticity of Finely Ground Minerals with Water," *ibid.*, **19** [4] 115–20 (1936); see also footnote 4, p. 89.

In order to disperse or peptize a given colloidal system of the electrocratic type, the presence of a high zeta potential on the particle has been known for a long while to accomplish this phenomenon. The discussion of clay plasticity in section III has shown that when sodium ions serve as the countercharges a repulsion force of some magnitude will exist at the edge of the water hull (see Fig. 3). This is another way of stating that the zeta potential is high. The best dispersion of a clay–water system, accordingly, will occur when sodium ions are present in the exchange positions. Because of the high zeta value, it will also be possible to use a higher concentration of the charged solid particles in a slurry and still retain the flow properties of a relatively dilute slip. Theory again is in accord with practical results, and in the production of these high specific gravity slips, the clay is converted to the sodium form by means of sodium silicate and (or) sodium carbonate.

There is a phase of deflocculation of casting slips which colloidal chemistry indicates should be considered although its importance has not been fully realized. It has been pointed out[7] that stability of electrocratic systems is controlled by the anion present in the medium, and therefore to render a system unstable colloidally, an anion possessing the same charge but opposite the one preferentially adsorbed should be used. Anions, which are strong acid formers such as the sulfate, chloride, or nitrate ions and opposite the hydroxyl ion in the Hofmeister series, would fall into the category of ions which might interfere with the stability of a deflocculated slip. A more complete deflocculation of casting slips has been found possible if the sulfate ion is absent. A relatively simple treatment, based on the fact that rendering these substances insoluble removes the ions from the system, is being used with success. Barium carbonate precipitates the sulfate radicle, whereas several reagents may be used to render the chloride ion ineffective and thereby to increase materially the flow properties of casting slips.

One drawback to the use of the casting process for fabricating ware today is that the complicated shapes being made require a certain amount of finishing, usually in the form of pasting or "sticking" two or more separately cast pieces to the main body. This sticking process demands a cast piece with good plasticity. Clay in the sodium form has been shown to be the least plastic. Inasmuch as the casting slip contains clay in the sodium form, the cast piece would be composed of clay in the sodium or least plastic form, because the only change occurring in the system during casting is the removal of water. If, by some manipulation, it were possible to employ first the fluidity of the sodium clay in pouring the slip and then to convert the sodium clay to a more plastic form during the casting process so that this clay form could be utilized in the subsequent operations, the limitations of fabricating ceramic ware by this process would be alleviated.

The results obtained in the laboratory during a study of this subject[8] indicate again the value of colloid chemistry to the ceramic industry. The treatment of porous molds with solutions of calcium or aluminum chloride caused an exchange reaction between the di- or tri-valent ions of the mold and the sodium ions of the clay. This reaction left the clay in a more plastic condition than that produced by a pure dewatering operation. Such a reaction, furthermore, was found to constitute a casting mechanism and did not require a mechanical removal of the water. In other words, the exchange of sodium ions for aluminum or calcium ions so alters the flow properties of the system that the slip which is introduced and displays high mobility becomes a stiff and rigid mass merely by virtue of this reaction. Colloidally speaking, a sol-gel transformation occurs simultaneously with the exchange reaction, which goes to such an extreme as to constitute a casting mechanism with no change in the percentage of water of the system. To the ceramist, such a casting mechanism has many advantages, the principal one being that if casting can be carried out without water removal, then no volume change will occur because shrinkage is a function of the water lost during the process. The benefits to be derived from such a casting process are not difficult to visualize.

V. Conclusions

The national emergency has resulted in an increased demand for many ceramic goods. Although the importation of foreign clays had been on the decline even before the international crisis, today this source of supply is not entirely dependable. For this reason alone, it is necessary to find a domestic source for essential war work for those plants which may have employed foreign clays. In addition to this factor is one dealing with the development of new processes and improved techniques in an attempt to reduce waste and losses and also to speed up production. Colloid chemistry will do much toward solving both of these problems.

Looking at the future development of the ceramic industry in a longer perspective, it is difficult to see the science of colloids taking any minor role. This paper has attempted to bring forth the fact that in a few brief years colloidal chemistry has aided this industry in a material way and that it will continue to do so is not questioned at this time.

Acknowledgment

The section on plasticity represents information which was obtained jointly with E. A. Hauser, whereas data on the deflocculation and casting mechanisms of clay were obtained jointly with F. H. Norton.

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[7] (*a*) E. A. Hauser and S. Hirshon, "Behavior of Colloidal Suspensions with Electrolytes," *Jour. Phys. Chem.*, **43**, 1015–36 (1939); *Ceram. Abs.*, **19** [6] 146 (1940).
(*b*) A. L. Johnson and F. H. Norton, "Fundamental Study of Clay: II, Mechanism of Deflocculation in the Clay–Water System," *Jour. Amer. Ceram. Soc.*, **24** [6] 189–203 (1941).

[8] A. L. Johnson and F. H. Norton, "Fundamental Study of Clay: III, Casting as a Base-Exchange Phenomenon," *ibid.*, **25** [12] 336–44 (1942).

FITTING GLAZES TO CERAMIC BODIES*

By H. G. Schurecht

Abstract

In fitting glazes to bodies, conditions of manufacture and service must be considered. Crazing tests for glazed ware to be used under different types of service are described, and new data are given pertaining to fitting glazes to ceramic bodies.

I. Introduction

Fitting a glaze to a body may be defined as selecting a glaze that will not craze, shiver, or peel under the conditions of manufacture or service. A glaze may fit a body under certain conditions of manufacture and service but fail when these conditions are altered. Porous glazed ware, for example, may craze badly when it is exposed to weathering but remain free from crazing if it is used indoors in a dry atmosphere. A glaze, furthermore, may be well adapted to a body if it is fired under oxidizing conditions but craze if fired under reducing conditions. Many such cases might be cited.

The purpose of this report is to describe methods of fitting glazes to bodies under varying conditions. A selected survey of the literature on this subject as well as new work done by the writer is included.

II. Methods for Determining Stresses Between Bodies and Glazes

(1) Flat-Plate Test

Hagar and Schofield[1] used a flat plate or tile to determine stresses between glazes and bodies. A specimen, 4 by 2 by $^3/_{16}$ in., may be used, and the warpage of the bisque ware may be determined first with the type of apparatus shown in Fig. 1. It is then glazed on one side and fired, and the warpage is again measured. If the warpage on the glazed side is concave, the glaze is in tension and is subject to crazing. If the warpage is convex, the glaze is under compression and may shiver or peel. Mild compression of the glaze is desirable because a certain amount of moisture expansion will develop in the body without causing the glaze to craze.

This method is comparatively simple, and a large number of samples may be tested in one firing. The warpage can be measured quickly, and the method is accurate for two-fire specimens. It cannot be used for one-fire ware, however, because warpage of the raw body during firing may introduce an error.

(2) Strength Test

Several investigators[2] have shown that the glaze influences the strength of ceramic bodies. The writer used strength tests on glazed bars to fit a body to a salt glaze. The flint content of the body was varied from 0 to 50% to change the body from a low-expansion body, which causes crazing, to a high-expansion body, which causes shivering. The glazed bars with 20% of flint were found to be the strongest, which indicates that this body has the best glaze fit (Fig. 2). If the glaze is in tension or compression, it tends to weaken the body; the strength is therefore greatest when the glaze is neither in tension nor in compression.

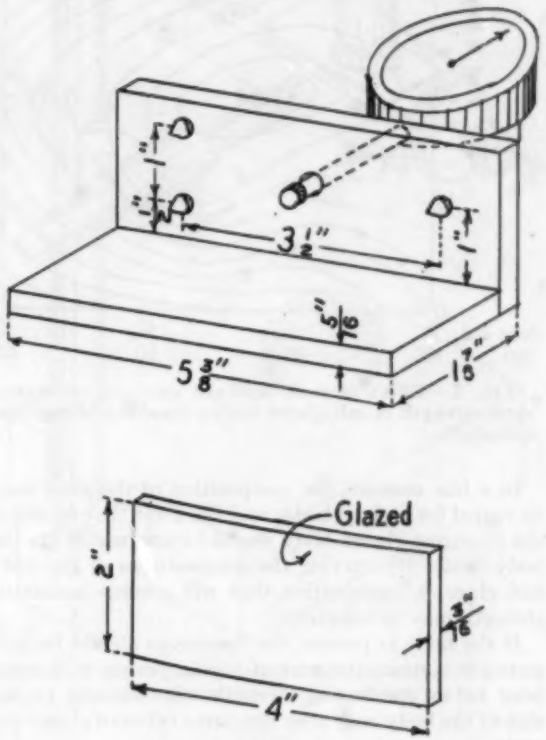

Fig. 1.—Flat plate glaze stress test.

* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 23, 1942. (White Wares Division.) Received September 23, 1942.

[1] H. Z. Schofield, "Study of Replacement of Cornwall Stone by Talc and Feldspar in a Wall-Tile Body," *Bull. Amer. Ceram. Soc.*, **16** [5] 203–204 (1937).

[2] (*a*) E. Gerold, "Influence of Glaze on Physical Properties of Porcelain," *Hermsdorf-Schomburg Mitt.*, No. 15, pp. 395–497 (1925); *Keram. Rundschau*, **33**, 188-90 (1925); *Ceram. Abs.*, **4** [6] 169–70 (1925).

(*b*) H. Handrek, "Importance of Glazes for Safe Porcelain Insulators," *Hermsdorf-Schomburg Mitt.*, Nos. 29–30, pp. 879–93 (1926); *Ceram. Abs.*, **6** [9] 392 (1927).

(*c*) D. H. Rowland, "Recent Improvements in High-Voltage Insulator Design," *Gen. Elec. Rev.*, **33**, 384–87 (1930).

(*d*) L. E. Thiess, "Influence of Glaze Composition on Mechanical Strength of Electrical Porcelain," *Jour. Amer. Ceram. Soc.*, **19** [12] 70–73 (1936).

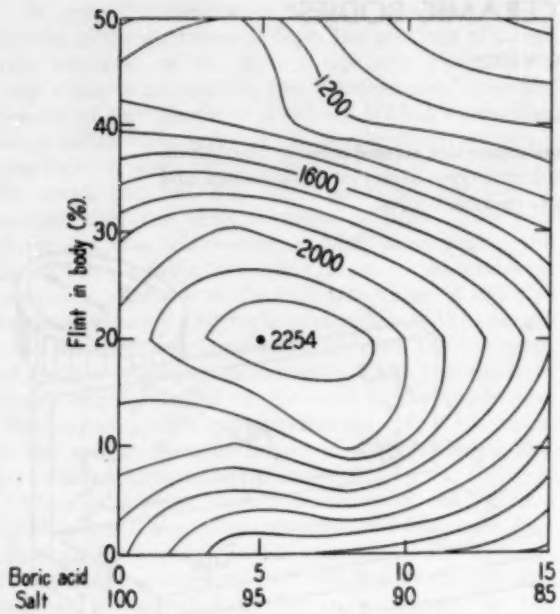

FIG. 2.—Effect of boric acid-salt mixtures on transverse strength of salt-glazed bodies (modulus of rupture indicated).

In a like manner, the composition of the glaze may be varied for a given body, and the glaze that produces the strongest glazed body would be one which fits the body best. By varying the compositions of the body and glaze, a combination that will possess maximum strength may be selected.

If the body is porous, the specimens should be subjected to a steam pressure of 150 lb. per sq. in. for one hour before conducting strength tests because expansion of the body may alter the stress between glazes and body.

The strength-test method of fitting glazes to bodies may be employed on one-fire and two-fire ware, but a large number of specimens must be tested, which is time consuming. Inexpensive apparatus may be used, however, and the effect of glazes on the strength of the ware may be measured directly.

(3) Deflection of Glazed Bars at Low Temperatures

Steger[3] measured the fit between body and glaze by glazing one side of a bar, 260 by 20 by 3 mm. in size, and heating it to 800°C. (Fig. 3). As the furnace is heated, the stresses resulting from differences in expansion of glaze and bar causes the bar to deflect until 800°C. is reached; the glaze then becomes plastic and the stresses are zero. If the bending of the bar is below zero (as shown in Fig. 3), the glaze is in tension and may craze; if it is above the zero line, the glaze is in compression.

[3] (*a*) W. Steger, "Strain in Glazed Ware and Its Detection," *Ber. deut. keram. Ges.*, **9** [4] 203–15 (1928); *Ceram. Abs.*, **7** [9] 625 (1928).

(*b*) W. Steger, "Measuring Tension in Fired Ceramic Mixes," *Ber. deut. keram. Ges.*, **11** [3] 124 (1930); *Ceram. Abs.*, **10** [3] 206 (1931).

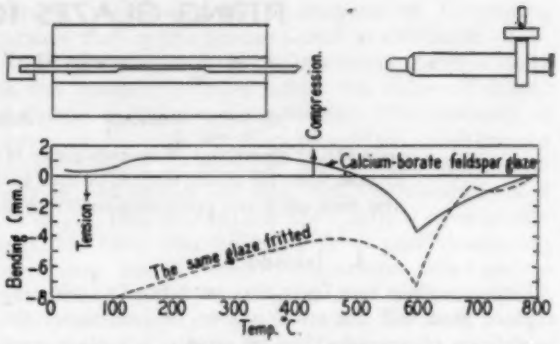

FIG. 3.—Steger method of determining stresses between glazes and bodies.

Morgan[4] modified this test by mounting the specimens vertically instead of horizontally, and the deflection was read on a scale, graduated to 0.1 mm., with a magnifying glass.

This test was further modified by Blakely[5] by using the tuning-fork method (Fig. 4). Two glazed bars instead of one are employed in this test. The deflection during firing is obtained by measuring with a telescope the distances between the free ends of the bars at different temperatures. Cut rings may also be used for deflection tests. This method will be described more fully.

The deflection test has proved to be satisfactory as a laboratory test for studying stresses between bodies and glazes during heating and cooling but it is a time-consuming method.

(4) Microscopic Method

A fairly thick section (about $^1/_{16}$ in. thick) is cut from the glazed ware perpendicular to the glazed surface. This is mounted on a glass slide and examined under polarized light with a gypsum plate. An unstressed glaze would be isotropic, whereas a stressed glaze would be anisotropic. The birefringence caused by the stressed glaze is measured with a Berek compensator.

The slow ray of the tint plate is aligned with the different quadrants. If the quadrant changes to a blue color, the glaze is in tension; if it changes to a yellow color, it is in compression; and a change to pink color usually indicates no stress.

A Berek compensator, inserted in the tube of the microscope, is rotated until extinction occurs, and the stress in the glaze is calculated by the formula[6] given in equation (1).

[4] W. C. Bell, "Evaluation of Glaze-Fit Test Methods," *Jour. Amer. Ceram. Soc.*, **23** [6] 163–66 (1940); see p. 163 for reference to Morgan test method.

[5] A. M. Blakely, "Life History of a Glaze: II, Measurement of Stress in a Cooling Glaze," *Jour. Amer. Ceram. Soc.*, **21** [7] 243–51 (1938).

[6] (*a*) R. W. Goranson and L. H. Adams, "Method for Precise Measurement of Optical Path Difference, Especially in Stressed Glasses," *Jour. Franklin Inst.*, **216** [4] 475–504 (1933); *Ceram. Abs.*, **13** [10] 254 (1934).

(*b*) A. J. Monack and E. E. Beeton, "Analysis of Strains and Stresses in Glass, I–IV," *Glass Ind.*, **20** [4] 127–32; [5] 185–91; [6] 223–28; [7] 257–62 (1939); *Ceram. Abs.*, **20** [3] 64 (1941).

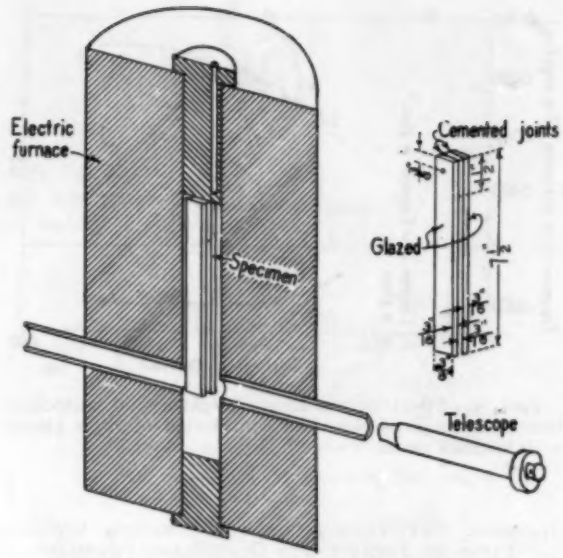

FIG. 4.—Apparatus used in Blakely double-pronged fork glaze stress test.

$$F = \frac{\Delta}{2.6E} \qquad (1)$$

F = stress (kg. per sq. cm.).
Δ = optical path difference (μ).
E = thickness (cm.).

Although this test is satisfactory for transparent glazes, it cannot be used for opaque glazes and engobes.

(5) Ring Test

Stresses between glazes and bodies are measured on rings which are 2 to 3 in. in diameter, 1/2 to 3/4 in. high, and 1/8 to 1/4 in. in wall thickness.[7] Rings with thin walls are used for vitreous bodies, and thicker wall rings for porous bodies. The rings may be pressed in a special iron mold, or they may be cast in plaster molds.

Two holes, 1/32 in. in diameter and 1/16 in. deep, are pressed in the upper rim of the rings about 1/4 in. apart while they are still plastic (this may be done with a pair of dividers). The rings are glazed only on the outside. After firing, small pieces of capillary glass tubing drawn out to a thread are cemented in the holes on the rim of the rings with a suitable cement, such as glycerine litharge or Glyptal cement. Small 0.004-in. shims of brass may also be cemented to the rims, and reference marks can be scratched on these with a razor blade.

The distance between the reference marks on the rings is measured with a micrometer microscope (Fig. 5). The rings are cut between the reference marks with a diamond or thin silicon carbide saw. The distance between the reference marks is again measured, and the expansion or contraction of the rings is calculated.

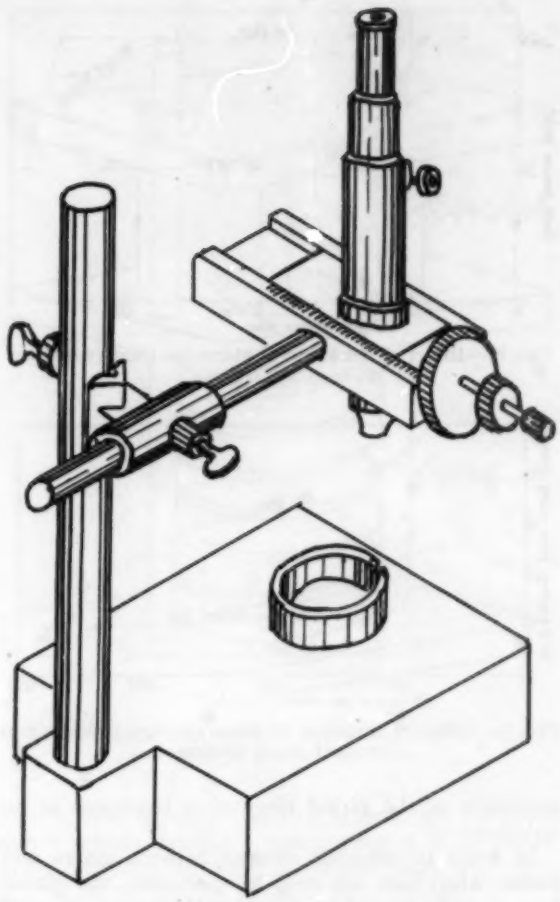

FIG. 5.—Micrometer microscope for measuring the expansion or contraction of rings.

If the ring expands, it indicates that the glaze is in tension and may have a tendency to craze; if the ring contracts, the glaze is in compression. Shivering or peeling may occur if the contraction is extra high. Mild compression is usually preferable because it allows the body to expand slightly during service without throwing the glaze in tension.

The ring test, which is a versatile method, may be used for one-fire and two-fire ware, for opaque as well as transparent glazes, and for fitting underslips and engobes to ceramic bodies. A large number of specimens can be fired in a small test kiln, and measurements can be made in a relatively short time.

The cut rings with chrome, nickel, or platinum reference lugs may be used to make deflection tests at low temperatures. The rings are placed in a small electric furnace, and measurements are made between the reference marks by means of a micrometer microscope, which is sighted on the specimens through a quartz glass window while they are being heated.

The cut rings may also be used to compare the moisture expansion of different bodies by noting the

[7] (*a*) H. G. Schurecht and G. R. Pole, "Method of Measuring Strains Between Glazes and Ceramic Bodies," *Jour. Amer. Ceram. Soc.*, **13** [6] 369–75 (1930).
(*b*) H. E. Davis and R. L. Lueders, "Simplification of Ring Method for Determining Glaze Stresses," *ibid.*, **15** [1] 34–36 (1932).
(*c*) W. C. Bell, see footnote reference 4.

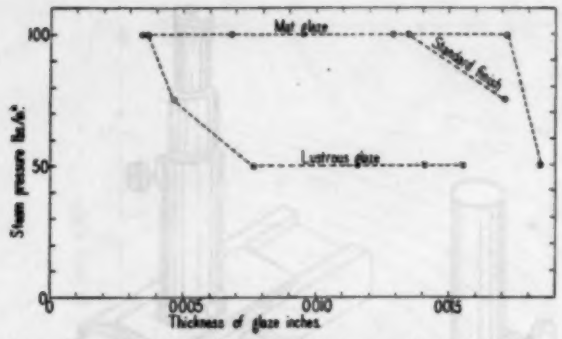

FIG. 6.—Effect of thickness of glazes on their resistance to moisture crazing.

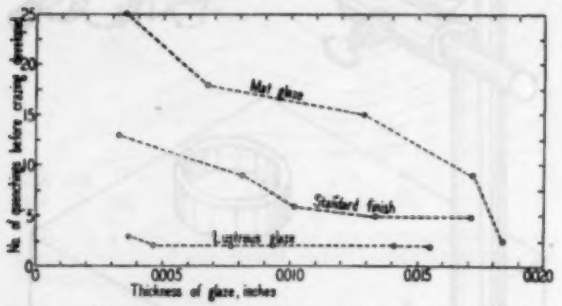

FIG. 7.—Effect of thickness of glazes on their resistance to thermal shock crazing.

expansion of the glazed rings after treatment in an autoclave.

In order to calculate stresses between glazes and bodies when bars are used as specimens, the glazed bars must be heated to the annealing temperature of the glaze to obtain the initial stress-free deflection of the bar. In the ring test, this is not necessary because the stress-free shape of the ring is the same as the original uncut ring. It is therefore unnecessary to heat the rings to red heat to determine the stress-free measurement on rings as required in the glazed bar tests.

III. Conditions of Manufacture

(1) Effect of Thickness

It is apparent from Figs. 6, 7, and 8 that the thickness of glaze application has considerable influence on glaze fit. On terra cotta bodies, the 0.010-in. thick lustrous glaze after firing crazed at 50 lb. per sq. in. when tested in the autoclave, whereas the same glaze at 0.0038-in. thickness did not craze until a pressure of 100 lb. per sq. in. was used (Fig. 6).

In thermal-shock crazing tests, a mat glaze 0.0183 in. thick crazed after 3 quenchings, and the same glaze at 0.0035-in. thickness first crazed after 25 quenchings (Fig. 7).

A lustrous glaze, applied thin, was found to be under less compression than a thicker application when measured by the ring stress test (Fig. 8.). After autoclave treatment, the thin glaze was again found to be in less tension than the thicker glaze.

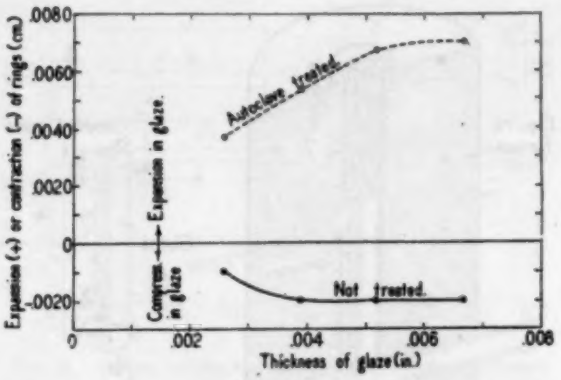

FIG. 8.—Effect of thickness of glaze and autoclave treatment on expansion and contraction of rings glazed with lustrous glaze.

TABLE I

STANDARD DRY THICKNESSES FOR SPRAYING VARIOUS TYPES OF TERRA COTTA GLAZES AND FINISHES

Glaze No.	Type of glaze or finish	Thickness (in.)
1	High-clay slips	0.009–0.011
2	Low-clay slips (standard finishes)	.009– .011
3	Satin mat glazes with underslip	
	(*a*) Underslip	.003– .005
	(*b*) Satin mat glaze	.018– .022
4	Mat glazes with underslip	
	(*a*) Underslip	.003– .005
	(*b*) Mat glaze	.014– .018
5	Lustrous glazes with underslip	
	(*a*) Underslip	.003– .005
	(*b*) Lustrous glaze	.022– .026
6	Mat glazes without underslip	.023– .027
7	Lustrous glazes without underslip	.032– .036

Table I gives the dry thickness measurements of the glazes and slips which were found to be satisfactory for use in the terra cotta industry. Two types of instruments are in use for measuring the dry thickness of a glaze. In the dial method (Fig. 9*A*), a small portion of the dry glaze is scraped from the body. By taking measurements on the glaze and on the bare body, the dry thickness of the glaze may be calculated. The bare portion of the body can then be covered with a daub of raw glaze unless the fired thickness of the glaze is also to be measured.

The fired thickness may be measured by scraping the dry glaze from a small portion of the body; after firing, the dial is allowed to rest alternately on the body and glaze, and the thickness is calculated as the difference of the two dial readings.

In the cutting method, a sliding chisel is used, which operates at an angle of 15° from the horizontal (Fig. 9*B*). By cutting through the glaze at this angle, the exposed thickness of the glaze is magnified 3.63 times. A scale on which the divisions are magnified 3.63 times is mounted on this brass block and is used for direct measurements of the thickness of the dry glaze. Direct measurements of the fired thickness may be made unless the glaze has a tendency to flow.

The increase in weight of the body or in a piece of sheet iron caused by spraying the glaze may also be

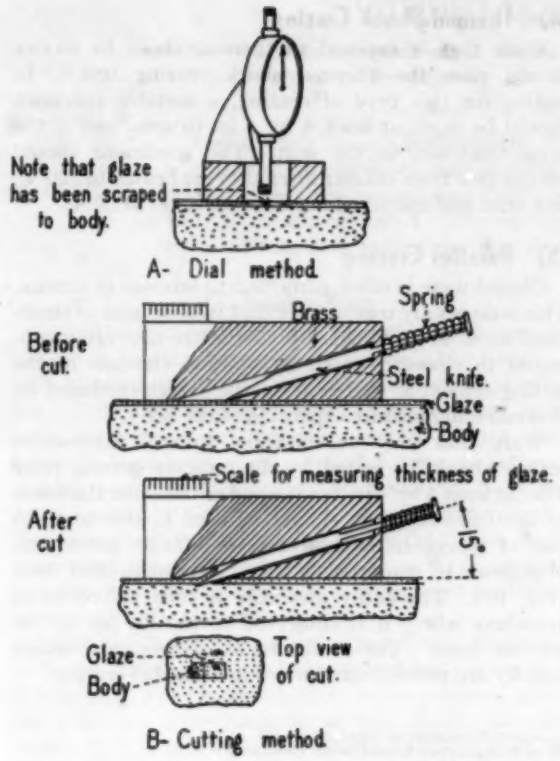

FIG. 9.—Methods of measuring thickness of dry glazes.

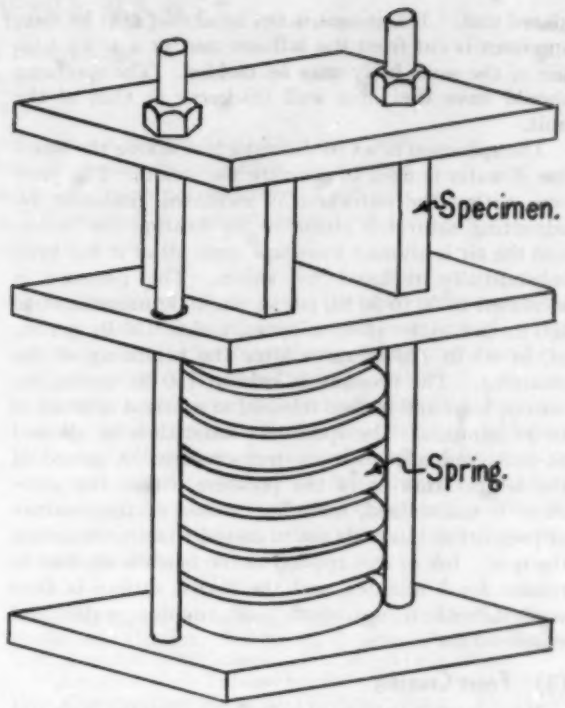

FIG. 10.—Apparatus used to test resistance to crazing produced by pressure on body.

used to measure glaze thickness. The thickness of sheet-steel enamels, for example, may be determined with a General Electric thickness gauge.

The methods described may be used as control tests inasmuch as they can be conducted in a short time. More accurate measurements of the glaze thickness may be made by peeling the glaze from the body with a glue or by measuring the thickness under a microscope.

The glaze may be peeled from the body by applying a glue* to the glaze surface. This glue, when dry, peels some of the glaze from the body, and the thickness may be measured with micrometer calipers on the peeled portions after any adhering body is removed.

The thickness may also be determined by cutting a section through the glaze and body with a diamond or silicon carbide saw and measuring the thickness with a micrometer microscope.

(2) Firing of Glaze

Crazing may occur when a glaze is fired under reducing conditions, whereas the same glaze, fired under oxidizing conditions, may be free from crazing.[8] If the ware is to be fired in a reducing kiln atmosphere, the glazed ware should be tested in a kiln atmosphere slightly more reducing than that in the kiln. The glaze should remain free from crazing when it is subjected to a steam pressure of 150 lb. for one hour.

IV. Different Types of Crazing

(1) Kiln Crazing

Kiln crazing develops in the kiln during cooling, and it is usually caused by a greater contraction of the glaze than that of the body. This type of crazing may be detected by applying ink or a dye to the glaze shortly after it is removed from the kiln. After allowing the ink or dye to remain on the finish for 5 minutes, it is washed off with a wet cloth and running water and then examined for crazing. Methods for overcoming this type of crazing have previously been reported.[9]

(2) Moisture Crazing

If ware is exposed to weather both in freezing and nonfreezing climates, it should be subjected to the autoclave test.[10] For an up-to-date test for moisture crazing, the specimens should consist of an entire

* A 20% solution of No. 1142 flake hide glue sold by the Russian Cement Co., Gloucester, Mass.

[8] H. G. Schurecht and G. R. Pole, "Some Special Types of Crazing," *Jour. Amer. Ceram. Soc.*, **15** [11] 632–37 (1932).

[9] H. G. Schurecht, How to Overcome Crazing in Ceramic Glazes, pp. 298–303. Ceramic Data Book. Industrial Publications, Inc., Chicago, Ill., 1941–1942; for abstract on this subject, see article from *Ceram. Ind.*, **37** [2] 44–49 (1941); *Ceram. Abs.*, **21** [1] 18 (1942).

[10] (*a*) H. G. Schurecht, "Methods for Testing Crazing of Glazes Caused by Increases in Size of Ceramic Bodies," *Jour. Amer. Ceram. Soc.*, **11** [5] 271–77 (1928).

(*b*) H. G. Schurecht and G. R. Pole, "Effect of Water in Expanding Ceramic Bodies of Different Compositions," *ibid.*, **12** [9] 596–604 (1929).

glazed unit. If this unit is not available, a 4- by 4-in. specimen is cut from the full-size unit or a 4- by 4-in. tile of the same body may be molded. The specimen should have the same wall thickness as that of the unit.

The specimen is set in the autoclave above the water line if water is used to generate the steam. The pressure within the autoclave is increased gradually by admitting saturated steam or by heating the water, and the air is allowed to escape until all of it has been substantially replaced by steam. The pressure is increased to 20 to 50 lb. per sq. in. in 30 minutes, 60 to 100 lb. per sq. in. in 60 minutes, and to 150 lb. per sq. in. in 80 to 120 minutes after the beginning of the steaming. The pressure is held at 150 lb. per sq. in. for one hour and is then released in a period of from 10 to 30 minutes. The specimens must then be allowed to cool gradually to room temperature. A record of the temperature or of the pressure within the autoclave is maintained, including values of temperature or pressure at intervals not to exceed 10 minutes during the test. Ink or dye applied to the finish is allowed to remain for 5 minutes, and the glazed surface is then washed with a wet cloth and running water and examined for crazing.

(3) Frost Crazing

If the ware is to be used in freezing climates, it should pass the frost-resistance crazing test.[8] Suitable specimens of the glazed ware should be soaked in water for 48 hours and frozen at −15°C. for 20 hours. They are then thawed by placing them in water at 20°C. for 4 hours after which they are again frozen. The glaze should remain free from crazing after it has been subjected to twenty-five freezing and thawing cycles.

(4) Thermal Shock Crazing

Ware that is exposed to thermal shock in service should pass the thermal shock crazing test.[11] In testing for this type of crazing, a suitable specimen should be used, at least 4 by 4 in. in area and of the same thickness as the unit. The specimens should remain free from crazing after they are heated to 120°C. in a drier and quenched ten times in water at 20°C.

(5) Parallel Crazing

Glazed ware is often subjected to stresses in service. This is especially true of ware that is to be used as structural units in buildings. Wall tile are also often subjected to stresses caused by volume changes in the setting cement as well as in the tile bodies produced by thermal and moisture expansion of the body.

Ware that may be subjected to such stresses in service should be tested by the pressure crazing test.[8] Tile, at least 4 by 4 in. in area and of the same thickness as the full-size units, should be used in this test. A pair of specimens is subjected to 1000 lb. per sq. in. of pressure by compressing a heavy spring against them (Fig. 10). The entire assembly is then placed in an autoclave where it is subjected to 150 lb. per sq. in. for one hour. The craze cracks in this case, which usually are parallel, are known as "parallel crazing."

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[11] H. G. Schurecht and D. H. Fuller, "Some Effects of Thermal Shock in Causing Crazing of Glazed Ceramic Ware," *Jour. Amer. Ceram. Soc.*, **14** [8] 565–71 (1931).

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VITRIFIED CORDIERITE BODIES *

By L. E. Thiess

Abstract

Twenty-eight ceramic bodies of the three-component system, $MgO \cdot Al_2O_3 \cdot SiO_2$, with additions of various fluxes, such as feldspar, beryl, spodumene, nepheline syenite, and other glassforming compositions and their vitrification range between cone 13 and cone 15 have been investigated. The electrical and mechanical properties, thermal expansion, and resistance against electrical power arcs are given.

I. Introduction

It has been known for some time that fired ceramic bodies of the three-component system, $MgO \cdot Al_2O_3 \cdot SiO_2$, have unusually low thermal expansion characteristics. It is only in recent years, however, that such bodies have found commercial use as high-tension insulators or have been recommended for use as ceramic cooking ware. Although such compositions have become known in Europe under various trade names, they have been mentioned in the United States more appropriately as "cordierite bodies,"[1] owing to the fact that the fired structure consists essentially of cordierite crystals ($2MgO \cdot Al_2O_3 \cdot 5SiO_2$).

Geller and Insley,[2] in following up some earlier work by Singer and Cohn,[3] found that a fired body composed of talc 43%, Florida kaolin 35%, and corundum 22%, and a similar body made up of talc 39.5%, Georgia kaolin 47.2%, and calcined alumina 13.3%, fired to 1350°C., consisted essentially of cordierite crystals. The thermal expansion range between 25° and 100°C. was 0.2×10^{-6} to 0.7×10^{-6}; between 25° and 600°C. it was 0.9 to 1.9×10^{-6}. The fired bodies were porous, and the fired color ranged from light buff to gray. A series of porous talc-clay-corundum bodies, fired at cones 10 to 11 for use in electrical refractories, has been reported by the writer in an earlier investigation.[4] The bodies had high resistance to thermal shock (780°C. to cold water) and the thermal expansion was very low. Krause and Jaeckel[5] also investigated a number of talc-clay-alumina bodies, fired from cones 4 to 14. The bodies remained porous up to the sudden fusion point, and no safe range of vitrification was found. The maximum cordierite formation and lowest thermal expansion occurred between cones 12 and 14.

To make such low-expansion bodies available for high-tension insulation, alkalis in the form of feldspar, Fe_2O_3, and other heavy metal oxides and red-firing clays were introduced to widen the firing range.[6] Vitrified cordierite insulators were thus produced in Germany in 1930, and their unusual resistance to power arcs and thermal shock was pointed out.[7]

Fig. 1.—Firing tests of cordierite bodies Nos. 1 to 10; top row, cone 13; middle row, cone 14; and bottom row, cone 15.

Fig. 2.—Firing tests of cordierite bodies, Nos. 11 to 19; top row, cone 13; middle row, cone 14; and bottom row, cone 15.

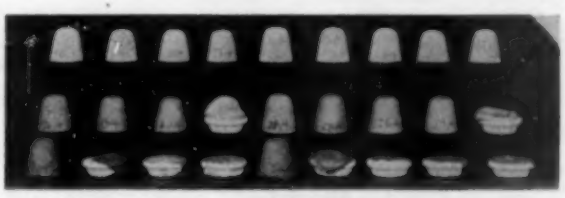

Fig. 3.—Firing tests of cordierite bodies, Nos. 20 to 28; top row, cone 13; middle row, cone 14; bottom row, cone 15.

* Received September 12, 1942.

[1] (*a*) H. Thurnauer, "Review of Ceramic Materials for High-Frequency Insulation," *Jour. Amer. Ceram. Soc.*, **20** [11] 368–72 (1937).

(*b*) H. Thurnauer, "Cordierite Gives Low Thermal Expansion in Ceramic Bodies," *Ceram. Ind.*, **29** [5] 362–64 (1937); *Ceram. Abs.*, **17** [11] 358 (1938).

(*c*) For review of the European special materials, see abstract for H. Handrek, *Ceram. Abs.*, **14** [9] 234 (1935).

[2] R. F. Geller and Herbert Insley, "Thermal Expansion of Some Silicates of Elements in Group II of the Periodic System," *Bur. Standards Jour. Research*, **9** [1] 35–46 (1932); *Ceram. Abs.*, **11** [10] 542 (1932).

[3] Felix Singer and W. M. Cohn, "New Ceramic Bodies: Composition and Expansion Behavior, I–II," *Ber. deut. keram. Ges.*, **10** [6] 269–84 (1929); *Ceram. Abs.*, **8** [11] 824 (1929).

[4] L. E. Thiess, "Steatite Ware as Ceramic Furnace Material," *Sprechsaal*, **65** [30] 549–52 (1932); *Ceram. Abs.*, **11** [11] 575 (1932).

[5] O. Krause and E. Jäckel, "Talc (Steatite)-Containing Bodies of Three-Component System $MgO \cdot Al_2O_3 \cdot SiO_2$," *Ber. deut. keram. Ges.*, **15** [9] 485–500 (1934); *Ceram. Abs.*, **14** [6] 145 (1935).

[6] Ernst Albers-Schönberg, Hochfrequenzkeramik (High-Frequency Ceramic Products), p. 23. Theodor Steinkopf, Dresden, 1939; *Ceram. Abs.*, **18** [11] 314 (1939).

[7] "Arcproof High-Tension Insulators Made from Sipa, a New Construction Material," *Stemag. Nachr.*, **10**, 14–26 (1933).

TABLE I

COMPOSITION, FIRED COLOR, AND WATER ABSORPTION OF CORDIERITE BODIES

(*A*) Feldspar Series (composition (%))

Body No.	1	2	3	4	5
Talc	43	42	42	40	36
Ball clay	35	34	32	30	29
Alumina	22	21	20	20	19
Feldspar		3	6	10	16
Cone 13					
Color	Cream	Cream	Cream	Light gray	Gray
Absorption (%)	13.0	8.5	3.2	2.1	0.0
Cone 14					
Color	Buff	Buff	Gray	Buff	Gray
Absorption (%)	9.9	6.1	0.2	0.0	0.0
Cone 15					
Color	Buff	Buff	Gray	Gray	Gray
Absorption	Fused	Fused	Fused	Fused	Fused

Body No. 5 showed some glaze development at cone 13, and it was completely covered with a glaze at cone 14.

(*B*) Spodumene Series (composition (%))

Body No.	6	7	8	9	10	11	12
Talc	40	36	42	42	40	36	36
Ball clay	30	29	34	32	30	29	29
Alumina	20	19	21	20	20	19	19
Spodumene	10	16	1	1.5	3	5	8
Feldspar			2	4.5	7	11	8
Cone 13							
Color	Buff	Buff	Ivory	Cream	Cream	Light gray	Buff
Absorption (%)	20.8	19.7	7.1	4.9	3.6	0.0	11.9
Cone 14							
Color	Buff	Gray	Buff	Brown	Gray	Gray	Dark gray
Absorption (%)	0.0	Fused	5.3	1.7	0.0	0.0	0.0 (bloated)
Cone 15							
Color	Brown	Gray	Brown	Brown	Gray	Gray	Gray
Absorption (%)	Fused	Fused	Fused	Fused	Fused	Fused	Fused

(*C*) Beryl Series (composition %)

Body No.	13	14	15	16	17	18	19
Talc	40	36	42	42	40	36	36
Ball clay	30	29	34	32	30	29	29
Alumina	20	19	21	20	20	19	19
Beryl	10	16	0.6	1.2	2.0	3.2	8
Feldspar			2.4	4.8	8.0	12.8	8
Cone 13							
Color	Buff	Ivory	Ivory	Ivory	Cream	Ceram	Cream
Absorption (%)	8.2	21.0	13.8	16.3	14.8	7.0	13.1
Cone 14							
Color	Brown	Gray	Buff	Brown	Gray	Gray	Gray
Absorption (%)	0.0	Fused	3.9	0.0	0.0	Fused	Fused
Cone 15							
Color	Brown	Gray	Brown	Gray	Tan	Gray	Gray
Absorption (%)	Fused	Fused	Fused	Fused	Fused	Fused	Fused

(*D*) Feldspar-ZnO Series (composition %)

Body No.	20	21	22	23
Talc	42	42	40	36
Ball clay	34	32	30	29
Alumina	21	20	20	19
Feldspar	2.4	4.8	8	12.8
Zinc oxide	0.6	1.2	2	3.2

TABLE I (*concluded*)

(*D*) Feldspar–ZnO Series (composition %)

Body No.	20	21	22	23
	Cone 13			
Color	Ivory	Ivory	Light gray	Gray
Absorption (%)	11.4	3.3	0.0	0.0
	Cone 14			
Color	Buff	Tan	Tan	Light gray
Absorption (%)	9.2	0.0	0.0	Fused
	Cone 15			
Color	Tan	Tan	Tan	Gray
Absorption (%)	0.0	Fused	Fused	Fused

Body No. 23 at cone 13 is completely glazed over.

(*E*) Nepheline-Syenite Series (composition %)

Body No.	24	25	26	27	28
Talc	42	42	40	38	36
Ball clay	34	32	30	30	29
Alumina	21	20	20	20	19
Nepheline syenite	3	6	10	12	16
	Cone 13				
Color	Ivory	Ivory	Light gray	Light gray	Gray
Absorption (%)	8.9	5.6	0.9	0.0	0.0
	Cone 14				
Color	Buff	Buff	Gray	Gray	Gray
Absorption (%)	4.2	4.6	0.0	0.0	Fused
	Cone 15				
Color	Tan	Tan	Tan	Gray	Gray
Absorption (%)	Fused	Fused	Fused	Fused	Fused

Body No. 28 at cone 13 is completely glazed over.

Parmelee and Thurnauer[8] reported dense talc-clay-zirconia bodies fired to cones 14 to 15, having thermal expansions of 1.12×10^{-6} (25° to 100°C.) and 2.89×10^{-6} (25° to 900°C.). Barium and titanium, also investigated in such bodies, gave unsatisfactory results.

II. Object of Study

In the present investigation, the effect of various fluxes, such as feldspar ($K_2O \cdot Al_2O_3 \cdot 6SiO_2$), spodumene ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$), beryl ($3BeO \cdot Al_2O_3 \cdot 6SiO_2$), nepheline syenite ($0.75Na_2O$, $0.25K_2O$, $1.1Al_2O_3$, $4.5SiO_2$), and low fusible mixtures of feldspar-zinc oxide, on the vitrification behavior and other electrical and mechanical properties has been studied.

III. Experimental Procedure

The compositions of the bodies are shown in Table I, series (*A*) to (*F*). The raw materials used and their percentage compositions were as follows:

(1) Canadian feldspar (SiO_2 66.2, Al_2O_3 18.6, K_2O 12.8, Na_2O 2.1).
(2) Tenn. ball clay (SiO_2 54.8, Al_2O_3 33.6, (K, Na)$_2O$ 1.20, H_2O 11.9).
(3) California talc (SiO_2 61.2, MgO 30.8, Al_2O_3 0.72, H_2O 5.35).
(4) Calcined alumina (Al_2O_3) prefired at 1200°C.
(5) Beryl (SiO_2 62.0, Al_2O_3 22.5, BeO 11.9, (K, Na)$_2O$ 1.4, CaO 1.4).
(6) Nepheline syenite (SiO_2 60.2, Al_2O_3 24.1, Na_2O 10.5, K_2O 4.5).

Casting bodies were prepared in batches of 2000 gm. each by grinding the materials with the necessary water and electrolytes for two hours in ball mills.

Cups, cast from each body, were $3\frac{1}{2}$ in. high and $3\frac{1}{4}$ in. at the base, with an average wall thickness of $\frac{1}{4}$ in.; these cups were fired in a gas-fired muffle kiln in 16 hours under oxidizing conditions. Larger batches were made of some of the vitrified bodies for casting standard test pieces for electrical and mechanical tests. The results of the three firings at cones 13, 14, and 15, shown in Figs. 1, 2, and 3, indicate clearly the narrow firing range of this type of ceramic body.

TABLE II

ELECTRICAL AND MECHANICAL TESTS*

Body No.	Cone No.	Transverse strength (modulus of rupture, lb./in.^{2})	Compression strength (lb./in.^{2})	Dielectric strength (volts/mil)
5	13	9950	30,000	130
11†	13	8370	19,000	35
16†	$13\frac{1}{2}$	11,370	26,000	77
23	13	10,020	44,000	143
27†	13	7910	32,800	41
28	13	9130	39,000	148

* Values obtained with A.S.T.M. Standard Methods of Testing Insulation Materials, Serial Designation D–116–39.
† Test specimens, subjected to the dye-penetration test of 7500 lb. per sq. in., were found to be slightly porous.

[8] C. W. Parmelee and Hans Thurnauer, "Some Effects of Additions of Compounds of Zirconium, Titanium, Aluminum, and Barium to a Talc Body," abstracted in *Bull. Amer. Ceram. Soc.*, **14** [2] 69 (1935).

IV. Results

Table II gives the results of the electrical and mechanical tests of some of the vitrified bodies. The linear coefficient of expansion for the temperature range 25° to 650°C. was determined on a Leitz photographically registering dilatometer.[9] Small extruded cylinders, 2 in. long and 1/8 in. in diameter, were used for this test. The expansion curves, as presented in Fig. 4, have been plotted from the photographic recording made in this test. It is shown that the thermal expansion of these cordierite bodies is considerably lower than that of electrical porcelain (see Fig. 4).

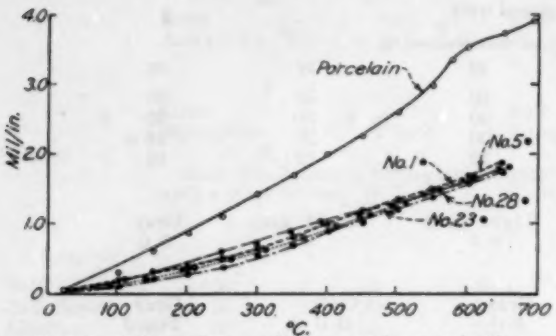

FIG. 4.—Thermal expansion curves for test bodies.

The glazing of cordierite bodies cannot be accomplished in the customary manner, as it is impossible to find high-fire glazes or glasses with the same low thermal expansion. An investigation showed that suitable, noncrazing, semimat glazes could be obtained by the use of glaze slips prepared from the same body mixed with coloring oxides. Inasmuch as some of the bodies (for example, Nos. 5, 23, and 28) are self-glazing, that is, they develop a glaze over the entire surface during firing, the oxides combine with this glaze and form a smooth finish on the surface of the fired body.

Another slip glaze was found to be suitable for this purpose, which had a chemical percentage composition of SiO_2 52.0, Al_2O_3 13.5, MgO 15.5, B_2O_3 3.2, Fe_2O_3 9.0, and Cr_2O_3 6.5, and gave a smooth semimat glaze. It was prepared from talc, ball clay, boric acid, and the coloring oxides.

V. Microscopic Examination

In a recent paper, Rigby and Green[10] show a photomicrograph of cordierite, which was prepared by heating talc, china clay, and alumina at 1420° to 1440°C. The cordierite crystals appear under the microscope (crossed Nicols ×75) as a large colorless prism giving straight extinction and having negative birefringence.

A microscopic examination by means of the powder method, made on the self-glazing body No. 28 and fired to cone 13 (1350°C.), shows that the ground mass consists mainly of rectangular-shaped crystals with some glass and amorphous substance. The crystals have a refractive index between 1.522 and 1.530 and show birefringence. They also exhibit parallel extinction and, where elongated, they have a negative optical character. In all these respects, these crystals may be identified as cordierite. Most of these crystals have inclusions, most of which are small and nondescript. There are some inclusions of higher refractive index and birefringence than the cordierite, and these may be corundum. There were a few crystals of cordierite showing a hexagonal cross section.

VI. Conclusions

The results of this investigation show that feldspar, nepheline syenite, and feldspar-zinc oxide, used as a flux in vitrified cordierite bodies, offer the best possibilities. Although it was also possible to obtain vitrified bodies with spodumene and feldspar and with beryl and feldspar, none of these developed self-glazing bodies; repeated firing tests, furthermore, showed that these bodies had too short a firing range for practical application.

The mechanical and electrical properties of some of the best bodies compare well with those obtained with regular feldspar-flint-clay bodies used for electrical high-tension work. The coefficient of thermal expansion for the vitrified cordierite bodies is considerably lower and the expansion curves are even and free from sudden changes resulting from the quartz inversion in regular electrical porcelain bodies. The thermal shock resistance of cordierite bodies is therefore very high, and power arc tests carried out on cordierite insulators showed that this material is far superior to regular electrical porcelain.

Acknowledgment

The author wishes to acknowledge his indebtedness to Louis Navias of the General Electric Research Laboratory for making the microscopic examination of fired cordierite body No. 28.

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GENERAL ELECTRIC COMPANY
SCHENECTADY, NEW YORK

[9] A. Metz, "Zeiss Dilatometer for Investigating Glasses," *Glastech. Ber.*, **16** [1] 19–20 (1938); *Ceram. Abs.*, **17** [6] 215 (1938).

[10] G. R. Rigby and A. T. Green, "Thermal Expansion Characteristics of Some Calcareous and Magnesian Minerals," *Trans. Brit. Ceram. Soc.*, **41** [5] 123–42 (1942); *Ceram. Abs.*, **21** [11] 249 (1942).

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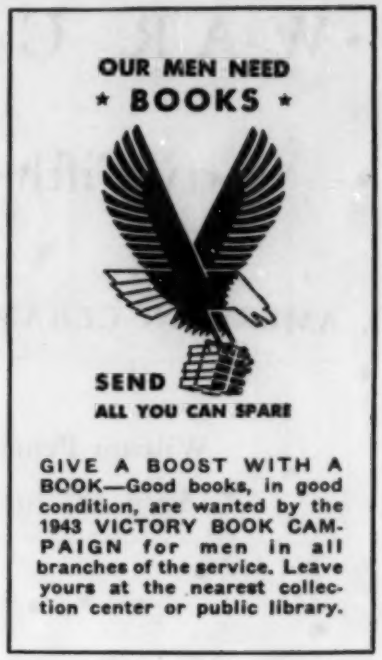
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Institute of Ceramic Engineers: H. G. Wolfram, Porcelain Enamel & Mfg. Co., Baltimore, Md. (1944)
Ceramic Educational Council: J. W. Whittemore, Virginia Polytechnic Institute, Blacksburg, Va. (1944)

* Date of expiration of term of office in parentheses.

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Chairman: Karl Kautz, Climax Molybdenum Co., First National Bank Bldg., Canton, Ohio
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Glass
Chairman: W. C. Taylor, Corning Glass Works, Corning, N. Y.
Secretary: S. R. Scholes, N. Y. State College of Ceramics, Alfred, N. Y.

Materials and Equipment
Chairman: J. F. McMahon, N. Y. State College of Ceramics, Alfred, N. Y.
Secretary: J. R. Kauffman, Allied Engineering Co., 29 Highland Drive, Milltown, N. J.

Refractories
Chairman: R. S. Bradley, A. P. Green Fire Brick Co., Mexico, Mo.
Secretary: W. R. Kerr, Armstrong Cork Co., Beaver Falls, Pa.

Structural Clay Products
Chairman: R. A. Shipley, National Fireproofing Corp., Pittsburgh, Pa.
Secretary: E. F. Theobald, Metropolitan Paving Brick Co., Canton, Ohio

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Chairman: F. C. Henderson, Royal China Co., Sebring, Ohio
Secretary: J. R. Beam, Universal Sanitary Mfg. Co., New Castle, Pa.

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Secretary: A. C. Jackson, The Claycraft Co., Columbus, Ohio

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